INSTITUTE OF METALS DIVISION

1938

A. I. M. E.

Louis D. Alpert

TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

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vol. 128
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Volume 128

INSTITUTE OF METALS DIVISION

1938

American Institute of Mining, Metallurgical, & Petroleum Engineers

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT MEETINGS HELD AT ATLANTIC CITY, OCTOBER 18–21, 1937 AND NEW YORK, FEBRUARY 14–18, 1938

PUBLISHED BY THE INSTITUTE
AT THE OFFICE OF THE SECRETARY
29 WEST 39TH STREET
NEW YORK, N. Y.

Notice

This volume is the twelfth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Atlantic City Meeting, Oct. 18–21, 1937 and the New York Meeting, Feb. 14–18, 1938. The complete list of publications and proceedings, including the present volume, is as follows:

1908–1911 *Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.

1912–1916 *Transactions* of the American Institute of Metals, Vols. 6–10.

1917–1918 *Journal* of the American Institute of Metals, Vols. 11–12.

1919–1926 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.

1927–1928 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A. I. M. E. TRANSACTIONS.

1929–1938 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 83, 89, 93, 99, 104, 111, 117, 122, 124 and 128, Institute of Metals Division.

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AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS
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PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

FOREWORD

This is the twelfth volume of the TRANSACTIONS devoted wholly to the Institute of Metals Division. The Division originated in 1907, when the American Brass Founders Association was formed with forty-seven charter members. In these thirty-one years progress has been rapid; the membership has increased greatly; the quality of the work recorded has reached a high standard; and the service accorded by the Division to its members and to industry has become recognized.

As in the preceding volumes, there are included here papers on a diversity of subjects. These, as time passes, reflect the trends in the development of the science. It has been and will doubtless remain the policy of the Division to accept for publication only papers of high quality. With the growth of the science, these are evidently becoming more highly specialized as the desire to obtain basic information on the behavior of metals and alloys leads the investigator to increasingly detailed studies.

Our Annual Lectures have reflected our desire to contribute to the development of the basic science of metals. The lecture by Prof. P. W. Bridgman, of Harvard University, on "The Nature of Metals as Shown by Their Properties under Pressure," printed in this volume, is an admirable example, and we must count ourselves fortunate indeed to have had the pleasure of listening to it and to be able to include it in the TRANSACTIONS.

Detailed studies of the mechanism of solid-solid reactions, which have been appearing in these volumes for the past several years, are again represented by papers on age-hardening, transformations, and diffusion. We may note also the increasing attention paid to the analysis of the mechanical properties, in which the same type of attack is manifesting itself. It has been only recently that the physical metallurgist has turned his attention to the science of the elasticity and plasticity of metals, and while a surprising number of familiar and apparently elementary phenomena remain to be explained, we may now confidently expect the metallurgist to provide the explanations, for while scientists in correlated fields have frequently made basic contributions to the science of metals, the well trained metallurgist, with his wide knowledge of metallic phenomena, is in an advantageous position to solve his own problems.

Often these several basic studies add little directly to the practical application of alloys but their success in unraveling the mysteries that surround these difficult subjects is providing the investigator with tools of thought, which make him far more competent to handle the more difficult technical problems of the day. An expanding science, an increasing understanding of basic processes, must inevitably be accompanied by an increasing technical proficiency. This is not new, but it is well to put ourselves in remembrance of it. The diversity of subjects, and the degree of specialization now required for advance, creates a difficulty for the reader of such a volume, for no one can be a specialist in each. This is unavoidable and can be met, in so far as a society such as this can meet it, only by an increasing use of symposia. The present volume includes a series of papers on powder metallurgy presented at a symposium at the February meeting this year; similar symposia on other subjects are planned for the future. The Institute feels that one of its important duties is to provide opportunities for its membership to familiarize itself with advances on the wide front of metallurgy, so that new scientific knowledge may find its application.

We are anticipating with great pleasure the visit of the members of the Institute of Metals and the Iron and Steel Institute of Great Britain, who will hold their meetings in this country in October this year, and who are planning also to attend our meetings. Several exchange papers have been arranged.

Much of the work entailed in choosing papers, in organizing meetings, and in assembling this volume has fallen upon Dr. D. K. Crampton, Chairman of the Papers and Programs Committee, and Dr. C. S. Smith, Vice-chairman of that committee, and to them must be given credit for the merit of the volume. The chairmen of the several committees deserve commendation for their efforts, particularly Dr. K. R. Van Horn, of the Membership Committee, who, with the able assistance of his committee, has exerted unusual efforts in this important work. It has been a pleasure, as Chairman of the Division, to work with all the committees and officers of the Division. Their counsel and cooperation have made the task of the chairman a pleasant one.

ROBERT F. MEHL, *Chairman,*
Institute of Metals Division.

PITTSBURGH, PA.
June 27, 1938.

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BYLAWS OF THE INSTITUTE OF METALS DIVISION

(As approved by the Board of Directors September 16, 1937)

ARTICLE I

Name and Object

Sec. 1. This Division shall be known as the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

Sec. 2. The object of the Division shall be to furnish a medium of cooperation between those interested in the metallurgy, fabrication and uses of the nonferrous metals and their alloys; to represent the A.I.M.E. in so far as nonferrous metallurgy is concerned, within the rights given in A.I.M.E. Bylaw XI., Sec. 1, and not inconsistent with the Constitution and Bylaws of the A.I.M.E.; to hold meetings for social intercourse and the discussion of nonferrous metallurgy; to stimulate the writing, presentation and discussion of papers of high quality on nonferrous metallurgy; to reject or accept such papers for presentation before meetings of the Division.

ARTICLE II

Members

Sec. 1. Any member of the A.I.M.E. of any class and in good standing may become a member of this Division upon registering in writing a desire to do so, but without additional dues.

Sec. 2. Any member not in good standing in the A.I.M.E. shall forfeit his privileges in the Division.

ARTICLE III

Funds

Sec. 1. The expenditure of the funds received by the Division shall be authorized by the Executive Committee of the Division.

ARTICLE IV

Meetings

Sec. 1. The Division shall meet at the same time and place as the Annual Meeting of the A.I.M.E., and at such other times and places as may be determined by the Executive Committee subject to the approval of the Board of Directors of the A.I.M.E.

Sec. 2. The annual business meeting shall be held within a few days before or after the annual business meeting of the A.I.M.E.

Sec. 3. At any meeting of the Division for which notice has been sent to the members of the Division through the regular mail at least one month in advance, a business meeting may be convened by order of the Executive Committee, and any routine business transacted not inconsistent with these Bylaws or with the Constitution or Bylaws of the A.I.M.E.

Sec. 4. For the transaction of business, the presence of a quorum of not less than 25 members of the Division shall be necessary.

ARTICLE V

Officers and Government

Sec. 1. The officers of the Division shall consist of a Chairman, two Vice-chairmen, Secretary and Treasurer. The office of Secretary and Treasurer may be combined in one person, if desired by the Executive Committee.

Sec. 2. The government of the affairs of the Division shall rest in an Executive Committee, in so far as is consistent with the Bylaws of the Division and the Constitution and Bylaws of the A.I.M.E.

Sec. 3. The Executive Committee shall consist of the Chairman, two Vice-chairmen, Past-chairman, Secretary, and nine members, all of whom shall be nominated and elected as provided hereafter in Article VII.

Sec. 4. The Chairman and Vice-chairmen shall serve for one year each, or until their successors are elected. Each member of the Executive Committee shall serve three years. The Chairman shall remain a voting member of the Executive Committee for one year after his term as Chairman.

Sec. 5. The Treasurer of the Division shall be invited to meet with the Executive Committee, but without ex-officio right to vote. He shall be appointed annually by the Executive Committee, from the membership of the Executive Committee or otherwise.

Sec. 6. The annual term of office for officers of the Division shall start at the close of the Annual Meeting of the Institute and shall terminate at the close of the next Annual Meeting.

ARTICLE VI

Committees

Sec. 1. There shall be six standing committees as follows: Papers and Programs Committee, Finance Committee, Data Sheet Committee, Membership Committee, Annual Lecture Committee and Annual Award Committee and such other Committees as the Executive Committee may authorize.

Sec. 2. It shall be the duty of the Papers and Programs Committee to secure the presentation of papers of appropriate character at meetings of the Division and of the A.I.M.E.

Sec. 3. It shall be the duty of the Finance Committee to inquire into and examine the financial condition of the Division and to consider proper means of increasing its revenue and limiting its expenses. The Finance Committee shall audit the accounts of the Division and report to the Executive Committee prior to the Annual Meeting of the Division. It shall render a budget to the Executive Committee estimating receipts and expenses for the ensuing year so that action can be taken on same at the first meeting following the Annual Meeting.

Sec. 4. It shall be the duty of the Membership Committee to encourage and solicit membership in the A.I.M.E. and in the Division in accordance with the Bylaws and Constitution of the A.I.M.E.

Sec. 5. It shall be the duty of the Annual Lecture Committee to arrange for the presentation at the time of the Annual Meeting of the A.I.M.E. of a lecture on a technical subject of particular interest to the Division and the A.I.M.E. as a whole. This lecture is to be known as the "Institute of Metals Lecture." This Committee shall make all arrangements, financial and otherwise, and render a complete report on same to the Executive Committee.

Sec. 6. The Chairman of the Division shall, subject to approval of the Executive Committee, appoint the Chairman and new members as required of the Committees referred to in Sec. 1.

Sec. 7. Appointments on standing committees shall be for terms of three years each with approximately one-third of the committee membership being appointed each year.

ARTICLE VII

Nominations and Elections of Officers and Committees

Sec. 1. Every year the Division shall elect a Chairman, two Vice-chairmen, a Secretary and three members of the Executive Committee.

Sec. 2. A Nominating Committee of five members of the Division shall be appointed by the Chairman of the Division subject to the approval of the Executive Committee.

Sec. 3. This Committee shall make its report to the Executive Committee not later than June 1.

Sec. 4. Any ten members of the Division may submit nominations for one or more offices to the Executive Committee not later than August 15, and the persons so nominated shall be included in the official ballot.

Sec. 5. The voting shall be by letter ballot.

Sec. 6. The ballots shall be counted by a committee of tellers appointed by the Executive Committee.

ARTICLE VIII

Amendments

Sec. 1. Proposals to amend these Bylaws shall be made in writing to the Executive Committee and signed by at least ten members. They shall be considered by the Executive Committee and announced to the members through the columns of Mining and Metallurgy, together with any comments or amendments made by the Executive Committee thereon. They shall be voted upon at the annual meeting of the Division in February or by letter ballot, as may be directed by the Executive Committee.

THE INSTITUTE OF METALS LECTURE

An annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
1923 Solid Solution. By Walter Rosenhain.
1924 The Trend in the Science of Metals. By Zay Jeffries.
1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
1927 Growth of Metallic Crystals. By Cecil H. Desch.
1928 Twinning in Metals. By C. H. Mathewson.
1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
1932 The Age-hardening of Metals. By Paul D. Merica.
1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
1935 Gases in Metals. By C. A. Edwards.
1936 Diffusion in Solid Metals. By Robert F. Mehl.
1937 Refractories. By R. S. Hutton.
1938 The Nature of Metals as Shown by Their Properties under Pressure. By P. W. Bridgman.

A.I.M.E. OFFICERS AND DIRECTORS

For the year ending February, 1939

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Louis Jordan

Assistant Treasurer
H. A. Maloney

Assistant to the Secretary
E. J. Kennedy, Jr.

Manager, "Mining and Metallurgy"
John T. Breunich

ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February.

There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmänstatten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. TRANSACTIONS (1931) **93**, 78–110.

1935 E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. TRANSACTIONS (1934) **111**, 264–292.

1936 Cyril S. Smith and W. Earl Lindlief: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. TRANSACTIONS (1933) **104**, 69–105.

1937 Arthur Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. TRANSACTIONS (1934) **111**, 94–112.

1938 William L. Fink and Dana W. Smith: Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy. TRANSACTIONS (1936) **122**, 284–293.

INSTITUTE OF METALS DIVISION

Established as a Division April 26, 1918

Chairman, Robert F. Mehl, Pittsburgh, Pa.
Past Chairman, Albert J. Phillips, Barber, N. J.
Vice-chairman, Robert H. Leach, Bridgeport, Conn.
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Lyall Zickrick,[1] Schenectady, N. Y.
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E. H. Dix, Jr., Chairman
H. A. Anderson
Zay Jeffries
W. M. Peirce
Clair Upthegrove

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[1] Until February 1939. [2] Until February 1940. [3] Until February 1941.

P. W. BRIDGMAN

Institute of Metals Division Lecturer, 1938

The Nature of Metals as Shown by Their Properties under Pressure

By P. W. Bridgman*

(Institute of Metals Division Lecture†)

It is characteristic of most scientific investigators that they are not satisfied with the discovery of new facts, no matter how curious or unexpected, but that along with the factual discovery there is a constant effort to understand. It appears that one's interest in, and satisfaction with, the discovery of an array of new experimental facts is enormously increased if one has at the same time a theory or hypothesis guiding one's expectation of what sort of new experimental discovery may lie around the corner. Conversely, as a theoretical physicist one's satisfaction with his theory is greatly enhanced if along with the development of the theory can go the discovery of new experimental facts, confirming or perhaps modifying the theory as it grows. Of course, there have been long arid stretches in the history of physics in which new data of unquestioned ultimate importance have piled up, without much inspiration or illumination in the way of understanding. For 50 years spectroscopy had such an arid history, but how irksome this was felt to be is plainly shown by the almost audible relief that greeted the first success by Bohr in injecting understanding into the situation, and by the fresh rush of experimenters into this field when the prospect of understanding had once been offered.

The investigations in the field of high pressure, which have occupied me for a long time,[1] until the last few years have been in very much the same sort of situation as spectroscopy before the advent of Bohr. A great many kinds of data were collected for a great many solid and liquid substances, and there could be no question of the importance of these data, because the uniform change of dimensions produced by hydrostatic pressure is perhaps the simplest conceivable type of alteration to which a body can be subjected. But except for a few isolated flashes, there was no theoretical illumination, so that it had to be to a large extent the enthusiasm of the collector that kept me going. However, within the last few years the wave-mechanics theory of solids has progressed so rapidly that

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* Hollis Professor of Mathematics and Natural Philosophy, Department of Physics, Harvard University, Cambridge, Mass.

† Presented at the New York Meeting, February 1938. Seventeenth annual lecture. Manuscript received at the office of the Institute March 8, 1938.

[1] Much of the earlier work will be found in my book: The Physics of High Pressures. New York and London, 1931. Macmillan, and Bell and Sons.

it is possible in many cases to calculate and even anticipate what the effect of pressure should be on a number of simple phenomena, and this possibility has for me greatly increased the interest of the experimental work.

At the same time, my experimental work has entered on a new phase, improvements in technique making it possible to reach pressures of 50,000 kg. per sq. cm., several fold higher than the previous range, and to measure a few simple properties in this range.[2] In this extended range there are very notable departures from linearity with pressure, so that the task of the theory is to reproduce whole curves instead of the straight lines that would have sufficed to reproduce experimental knowledge over a shorter pressure range. Theory is now proving adequate for this task in the simplest cases. In the following I shall try in the first place to give a summary of the new experimental knowledge with regard to metals which I have been able to gather in the extended pressure range, and in the second place to show how these data are fitting into the theoretical picture painted by wave mechanics. We must not make too great demands on the theory, which is still in the early stages of its development, but even so, I think that our theoretical understanding is immeasurably better than we would have dared to hope 15 years ago.

EXPERIMENTAL TECHNIQUE

First of all, I shall briefly describe the experimental technique, which recently has made it possible to extend the pressure range. It is, of course, well known that it is not possible to increase the resistance of a hollow cylinder to internal pressure by more than a strictly limited amount even by making the walls infinitely thick. The reason is that as the thickness is increased each new addition supports only a rapidly decreasing proportion of its share of the total stress, the stress being highly concentrated near the inner wall. Even in an infinitely thick cylinder the plastic flow point is reached at the inner surface when the internal pressure reaches a value of the order of magnitude of the elastic yield point in tension, and this plastic condition is rapidly propagated through the rest of the cylinder, and rupture occurs. This, then, represents the first natural limit to the strength of containers to internal pressure. This limit could be raised if the stress could be redistributed in some way through the walls, so that the parts of the walls more remote from the center could assume more nearly their proportional share of the stress. It is well known that this can be done by producing an initial compressive stress at the interior by shrinking tension hoops over the exterior, as in built-up guns, or in other ways. By this device the inner fibers of the walls at first make a negative contribution to the stress, so that the internal pressure is borne by the parts of the wall at some distance from the center. As pressure increases the main supporting region remains farther from the center than before, so that when the maximum pressure is reached the distribution of stress is more uniform, and the outer layers are supporting a larger share of the load. The limit to the increase of strength obtainable in this way is set by plastic flow in compression at the inner surface, for if the hoops are shrunk on too tightly the stress at the inner surface reaches the yield point in compression, and the cylinder collapses by plastic flow toward the center, before any external pressure at all is applied. This sets the second natural limit to the strength of containers to internal pressure; it is roughly of the order of magnitude of twice the first limit, or twice the plastic flow stress in tension. Until recently the upper limit of my pressures was this second limit. Subject to this limitation, measurements could be made with difficulty and uncertainty up to 20,000 kg. per sq. cm., but most of my measurements were limited to 12,000 kg. per sq. cm., where there is practically no difficulty from rupture of the apparatus.

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[2] P. W. Bridgman: *Phys. Rev.* (1935) **48,** 893; *Proc.* Amer. Acad. Arts and Sci. (1937–38) **72,** Nos. 2, 4, 5, 6.

We could evidently reach still higher pressures if, instead of allowing the maximum compressive stress at the interior to occur at the lowest pressures, when it is least needed, we could in some way neutralize the tension at the interior surface arising from the pressure by a compressive stress which increases in magnitude as the pressure becomes greater. This can be accomplished by applying to the external surface of the cylinder a pressure which rises in proportion to the increase of internal pressure. This is the method I have recently adopted; obviously it introduces considerable complication into the apparatus, but it is worth while because it proves possible in this way to increase the pressure range from 20,000 to 50,000 kg. per sq. cm.

The external pressure on the pressure vessel may be conveniently produced by giving the exterior a conical shape, like a rubber stopper, and pushing this cone into an external conical ring with a force which increases as the internal pressure increases. The simplest method of doing this is to make the force which drives the piston producing internal pressure at the same time thrust the cone into its external supporting ring, so that the external pressure rises automatically to keep pace with the internal pressure. This is suggested schematically by Fig. 1; with this apparatus many measurements have been made up to 50,000. There are, however, certain limitations imposed on the size of the vessels for which it is possible to produce the external pressure in this way; these

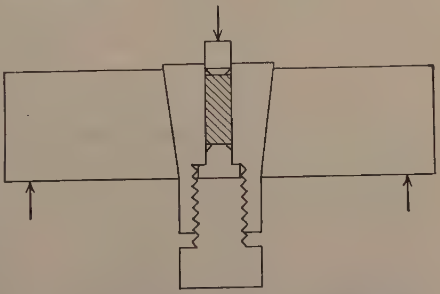

FIG. 1.—GENERAL PRINCIPLE OF METHOD BY WHICH PRESSURE IS AUTOMATICALLY PRODUCED ON EXTERIOR OF PRESSURE VESSEL AT SAME TIME IT IS PRODUCED ON INSIDE.

limitations arise from the limitations on angle imposed by friction. For experiments on a larger scale it proves to be necessary to reverse the orientation of the cone and drive the conical container into its supporting ring by a thrust exerted independently and in the opposite direction from the thrust on the piston. Apparatus constructed on this principle is suggested in Fig. 2.

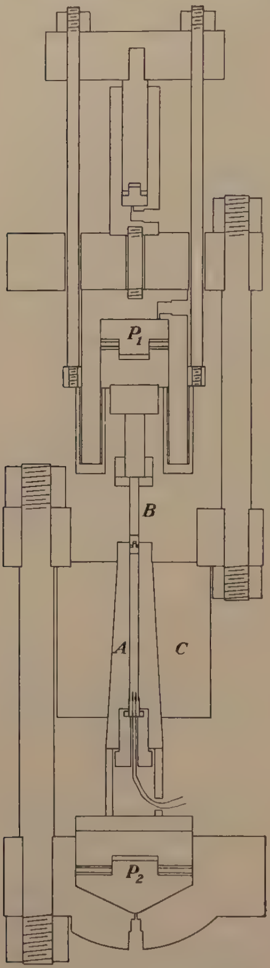

Fig. 2.—More elaborate apparatus for producing pressure independently on outside and inside of container.

Pressure is produced in interior of container A by piston B pushed by hydraulically actuated piston P_1. Pressure on outside of A is produced by hydraulically actuated piston P_2, which pushes A into heavy conical collar C. Upper and lower presses are held together with three tie rods each, shown as one for simplicity in drawing.

We have so far discussed the problem of making the pressure vessel strong enough to support internal pressure, and have not mentioned the method by which pressure is produced. Fortunately, heat-treated steel is much stronger in compression than in tension, so that up to the second stage of sophistication in our construction of pressure apparatus, pressure can be produced simply by the thrust exerted by an unsupported glass-hard steel piston. At the third stage of sophistication, however, the compressive strength of steel becomes inadequate, and in order to produce pressures comparable with the pressures which the vessel is capable of supporting we would either have to devise some method of supporting the piston or else construct it of a stronger material than steel. Most fortunately, the second and much simpler alternative can be adopted. Certain grades of Carboloy, the recently developed cemented carbide of tungsten and cobalt, have a compressive strength much higher than that of the best steel, and it is possible to use unsupported pistons of Carboloy that reach the highest pressures at present attainable. In this use of Carboloy I am extremely indebted to Dr. Zay Jeffries and the General Electric Co., who have most generously supplied me with this material.

The 50,000 kg. per sq. cm. reached with the present construction could not be much exceeded because of two different effects. A pressure of 50,000 is fairly near the practical limit of the Carboloy piston; in order to get much higher it will be necessary to find a material stronger than Carboloy, or else support the piston. In the second place, the pressure vessel is now very near the failing point because of longitudinal extension due to pressure on the curved surface, by what I have called the "pinching off" effect. In fact, a number of cases have occurred of such longitudinal failure—separation of the cylinder into two pieces on a plane perpendicular to the longitudinal axis as in tension. This can only be avoided by giving more complete external support to the pressure vessel—support at the ends as well as at the sides—and this will demand still more complicated apparatus.

Phenomena Studied

Three kinds of phenomena have been studied up to the present in the new pressure range above 20,000. Two of these depend on simple measurements of volume; changes of volume can be simply determined from the position of the Carboloy piston, and this can be easily measured in the first form of apparatus shown in Fig. 1 up to 50,000. The first and simplest of these volume phenomena is that of polymorphic transition from one modification of the solid to another. In almost all cases such a polymorphic transition is accompanied by a discontinuous change of volume, so the existence of these transitions is very simply established by plotting the position of the piston against pressure, the point of transition being indicated by a discontinuity on the plot. The magnitude of the volume change is given by the magnitude of the discontinuity. The pressure at which the change occurs is itself a function of temperature. A complete determination of the pressure of the change as a function of temperature, together with the magnitude of the change of volume, gives the data necessary for a complete thermodynamic characterization of the transition.

The second volume phenomenon is the volume itself as a function of pressure, from which the compressibility can be found at once. The volume change over a range of pressure is obviously connected with the motion of the piston as a function of pressure; in order to make the final calculations there are various corrections which have to be applied for the distortion of the apparatus, so that it is not as simple a matter to measure compressibility over the entire range of pressure as it is to determine a polymorphic transition by the discontinuity at a point, where most of the corrections drop out. Nevertheless it is possible to find the corrections with fair precision, and measurements have been made of the compressibility of a number of metals and other substances above 20,000.

The third kind of phenomenon is electrical resistance—the resistance of many metals may be greatly altered by an application of pressure. From a technical point of view, the measurement of resistance demands larger and more complicated apparatus than the measurement of volume. Electrically insulated leads must be got into the pressure apparatus, and pressure must be transmitted by an insulating liquid, so that the technical requirements on the apparatus become much more severe. For the resistance measurements the second form of apparatus described above has been used; the pressures attainable with this are for the present limited to 30,000 kg. per sq. cm. With this apparatus measurements have been made of the resistance of some 19 metals at two different temperatures.

1. *Polymorphic Transition under Pressure*

First, and apparently perhaps the most fundamental of all, is polymorphic transition under pressure. It is common knowledge that many

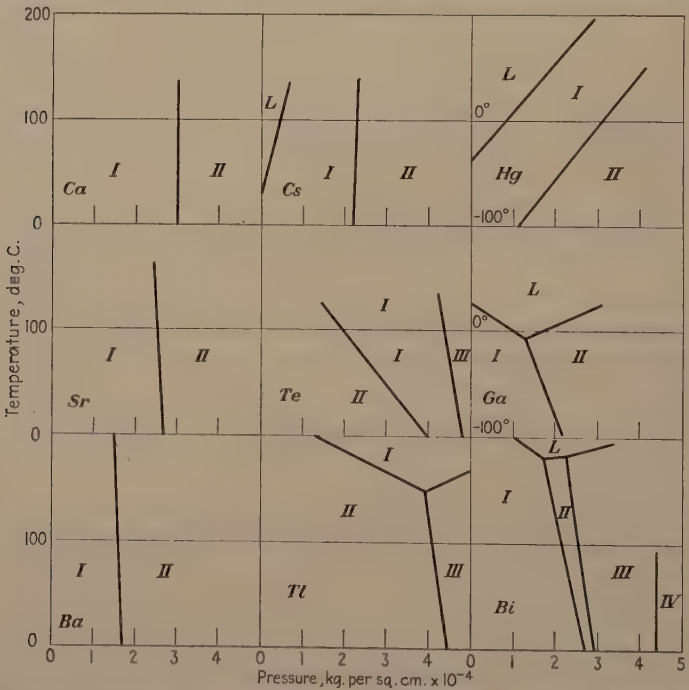

FIG. 3.—PHASE DIAGRAMS OF NINE METALS. NOTE DISPLACEMENT OF TEMPERATURE ZERO FOR MERCURY AND GALLIUM.

metals undergo transitions at atmospheric pressure with rise of temperature, and these phenomena are most important in the practical use of the metals. When one adds pressure to temperature as a second variable, the phenomena become very much richer, and many new modifications become capable of existence which never occur at atmospheric pressure at any temperature. Unfortunately, even if some of the new high-pressure modifications had useful properties, it would not be possible to utilize them in practical applications, for these transitions are reversible, and the metal reverts to its normal form when pressure is released. In Fig. 3 are collected the phase diagrams of nine metals for which the transition data have been determined by the volume discontinuity method. These metals all have comparatively low melting points, or at least are mechanically soft. There is good reason why the diagram of just this sort of metal has been determined experimentally. There is almost always a considerable internal frictional resistance to the change from one modification to another, and the frictional resistance may be so high that the change does not occur even though pressure may be raised far beyond the point at which the new phase, according to thermodynamics, becomes capable of replacing the old. The viscous resistance is less the higher the relative temperature; that is, the nearer the metal is to its melting point. One may suspect, therefore, that there may be many other examples of pressure polymorphism, besides those shown in the diagram, among the harder and higher melting metals. This does indeed seem to be true for if the metals are examined by the method of shearing stress, which cannot be described here except to state that shearing stress is much more likely to overcome internal viscosity than hydrostatic pressure, distinct evidence is found that still other metals of higher melting points, such as lanthanum, cerium, thorium and vanadium, pass into other modifications at high pressures.

We now discuss some of the individual metals shown in Fig. 3. Two of the most interesting examples of pressure polymorphism are bismuth and gallium. Both of these metals melt at atmospheric pressure with decrease of volume, a highly anomalous state of affairs, for which the only other well established example is ice to water. It has been known for some time that the anomalous relation between the volume of liquid and solid water is only more or less temporary and accidental, characteristic of low pressures, for at pressures above 2000 kg. per sq. cm. ordinary ice is replaced by a succession of more stable forms, all with greater density than the corresponding liquid. One would expect by analogy a similar state of affairs with bismuth and gallium, but until recently experimental search for the expected new forms had been unsuccessful. It appears that the reason was that the pressure had not been raised high enough. At pressures beyond 13,000 kg. per sq. cm. for gallium, and 25,000 for bismuth, the anticipated new forms have recently been found, so that at high pressures all substances now appear to have the normal relation between the volume of the solid and the liquid. Bismuth has at least three new high-pressure modifications; and, curiously enough, its phase diagram has rather striking resemblances to that of water.

The three alkali earth metals, calcium, strontium, and barium, all show polymorphism under pressure, and their phase diagrams are not dissimilar. Close examination shows, however, that the similarity is not as far-reaching as at first appears, for the structure of the normal modification of barium is body-centered cubic, whereas that of calcium and strontium is face-centered cubic. Since the face-centered cubic arrangement is close-packed, it suggests itself that barium is forced by pressure into the close-packed arrangement already assumed by calcium and strontium at atmospheric pressure. The high-pressure forms of calcium and strontium must then be something else, perhaps involving a rearrangement of the electrons at levels below the valence level in the atom, since the atomic arrangement is already close-packed. In any event, it is evident that the pressure transition in barium cannot be of the same character as that in calcium and strontium.

Among the phase changes listed above one would expect the most significant for theoretical purposes to be that of caesium, for this metal has a structure simple enough to enable calculations, which are of prohibitive difficulty for most other metals, to be carried through to a successful conclusion. This does, indeed, prove to be true, for Dr. John Bardeen, at Harvard, has succeeded in calculating not only that caesium should undergo a transition at high pressures, but has calculated also the approximate pressure at which the transition occurs and the magnitude of the volume change. A striking feature of the calculation by Dr. Bardeen was that it was made before the actual existence of the transition had been certainly established by experiment, and it was the stimulus of his calculation that led to the definitive experimental investigation. The structure of the atmospheric modification of caesium is body-centered cubic; at high pressure, calculation indicates that it is forced into a face-centered cubic arrangement, that is, a close-packed arrangement, which is what might be expected. The situation with regard to caesium is, however, very unusual. For many other substances, it is the low-pressure modification that has the close-packed arrangement—that is, the close-packed arrangement of spheres.

One might perhaps think that the first task for a theory of any particular crystalline substance would be to calculate the crystal system in which the substance crystallizes, and that then, having established the system, on the basis of it other physical properties could be calculated. If this were true, the prediction of the pressure at which to expect new forms would become one of the easiest tasks of the theory, but it turns out that the prediction of the precise crystal system is, in the present state of theory, one of the most difficult things that can be asked. At present, theory usually has to assume the crystal system as known from experiment, and then, in terms of the known system, it is an easier task to calculate other properties, such as compressibility or electrical resistance. The reason for this is that the energy differences, and also the differences of thermodynamic potential, which determine the relative stability of different possible phases, are usually very small compared with the total energy or thermodynamic potential, so that the total energy must be known with high precision in order to determine the differences of energy or potential, and so the transition parameters, with even moderate precision. Except for caesium, I do not know of any successful calculation that has been made for the metals. Even in the simplest case of all, that of the transitions of a number of ionic compounds from the NaCl to the CsCl type of structure, the calculations have proved too difficult to yield good values for the pressure of transition. The forces in ionic compounds are predominantly simple electrostatic inverse-square forces between the charged nuclei, superposed on repulsive forces when the ions get too close together. This repulsive force can be approximately calculated from other sorts of phenomena, but it turns out that assumptions about the repulsive forces which are adequate to account for the compressibilities, for example, fail when it comes to calculating the transitions. Thus, in *Physical Review* for August 15, 1937, May finds that in order to make his calculation eventually yield fairly satisfactory values for the transition temperatures of NH_4Cl and CsCl at atmospheric pressure it is necessary to alter arbitrarily one theoretically calculated force by a factor of 3.5 and another by a factor of 0.6. The phenomena of polymorphic transition thus appear from the theoretical point of view to be among the most delicate with which we are concerned. This delicacy is borne out from the experimental side by the observation that no other phenomenon shows such qualitative variation among substances closely related chemically, and which do show a high degree of similarity with regard to other properties.

2. *Volume Compression*

We next consider the second group of phenomena; namely, simple volume compression. On the experimental side, one of the most interesting features is the mere magnitude of the volume changes that can be produced by experimentally attainable pressures. Under ordinary pressures the volume changes of solids are negligible for most practical purposes, but at high pressures they may become very appreciable. In fact, in my previous range of pressures, up to 12,000 kg. per sq. cm., the volume changes were materially greater than the change on cooling from room temperature to absolute zero at atmospheric pressure. Of course, at 50,000 the changes must be importantly larger, but not larger in proportion, because if the volume were to continue to decrease with increasing pressure at the same rate it would presently pass through zero and become negative. To take an extreme case, if the compression of caesium continued at its initial rate, it would be squeezed out of existence at only 14,000 kg. per sq. cm. It is evident, therefore, that in general at high pressures the plot of volume against pressure must be convex toward the pressure axis, and one may expect, at least for the more compressible substances, that the departure from linearity is considerable. An adequate theory must reproduce not only the initial slope of the curve of volume against pressure, but also the entire course of the curve as a function of pressure.

The experimental determination of volume compressions up to 50,000 offers certain difficulties because of the various corrections for the distortion of the apparatus already suggested, so that up to the present acceptable measurements can be made only on the more compressible substances. I now have measurements for eleven of the more compressible metals, and for three other substances. In Table 1 are given the volumes of these metals as a function of pressure; the relative accuracy for the more compressible metals is naturally greater than for the more incompressible ones. These eleven metals include the five alkalies, which at present are of most interest to the theoretical physicist, and the three alkali earth metals, calcium, strontium, and barium, which also have a relatively high compressibility. The alkali metals are the most compressible of the metals; their compressibility increases with increasing atomic weight, reaching its maximum with caesium, which is compressed by a pressure of 45,000 kg. per sq. cm. to less than one-half its initial volume. One gets a rough idea of the departure from linearity by noticing in the table the compression at 20,000 as compared with that at 40,000; in general the compression at 40,000 is much less than twice that at 20,000. Among the alkalies, the deviation from linearity is greatest for caesium and least for lithium. This is a case of a general rule; namely, that the decrease of compressibility with rising pressure is greatest for those substances with the greatest absolute compressibility. In the alkali earth series the same sort of progression is found—compressibility increases with

TABLE 1.—*Compression of Eleven Low-melting Metals*

Pressure, Kg. per Sq. Cm.	$\Delta V/V_0$										
	Li	Na	K	Rb	Cs	Ca	Sr	Ba	In	Sn	Pb
5,000	0.043	0.071	0.116	0.164	0.182	0.031	0.047	0.045	0.012	0.010	0.012
10,000	0.074	0.117	0.183	0.233	0.271	0.058	0.075	0.086	0.024	0.020	0.023
15,000	0.101	0.148	0.230	0.279	0.326	0.082	0.099	0.121	0.035	0.029	0.032
								*			
20,000	0.125	0.182	0.268	0.316	0.372	0.103	0.122	0.159	0.045	0.038	0.041
					*						
25,000	0.145	0.209	0.301	0.345	0.420	0.122	0.136	0.186	0.054	0.048	0.050
30,000	0.165	0.233	0.329	0.371	0.438	0.139	0.155	0.209	0.064	0.057	0.058
35,000	0.184	0.254	0.353	0.393	0.464	0.155	0.172	0.230	0.073	0.066	0.065
40,000	0.202	0.273	0.375	0.413	0.487	0.171	0.188	0.250	0.082	0.075	0.072
45,000	0.218	0.290	0.396	0.431	0.507	0.188	0.204	0.269	0.091	0.084	0.079

* A polymorphic transition occurs in this interval.

increasing atomic weight and the relative decrease of compressibility with pressure increases also. It is to be noticed that the volume changes of caesium and barium listed in the table straddle a polymorphic transition. In both cases the volume change at the transition is small and the compressibility is not markedly affected by passing through the transition. In these two cases the change of lattice structure thus appears as a rather unimportant episode as far as other properties are concerned. This can be seen in another way from the fact that the energy difference between low-pressure and high-pressure caesium is only $\frac{1}{120}$ of the binding energy of caesium.

The theoretical calculation of compressibility has been attempted with varying degrees of success for a number of years. The first successful calculations were made for nonmetallic lattices of the simple NaCl type. A number of the simpler and more important properties of such lattices may be calculated from very simple assumptions about the law of force between the ions which occupy the points of the lattice; this force consists of a simple inverse-square electrostatic force between positive and negative ions, with a superposed repulsive force which increases very rapidly when the centers of the ions approach beyond a critical distance corresponding to what may roughly be called the size of the ions. This repulsive force was assumed for the simple calculations which were made at first to vary as some power of the distance to be determined empirically. For most of the simple ionic lattices it is approximately as the inverse ninth power. For recent wave mechanics this repulsive force is best represented by an exponential term. By means of this simple picture it is possible to calculate several of the more important properties of the lattice, such as the energy content and also the compressibility. However, it is only the initial compressibility that can be thus computed —the results are not at all in agreement with experiment when one attempts to calculate the change of compressibility with pressure; that is, the deviation from linearity of the curve of volume against pressure. More detailed considerations will be necessary therefore to reproduce the volume of the simple lattices as a function of pressure.

When it comes to calculating the compressibility of the metals, the nature of the structure and of the forces is importantly modified, and other methods of calculation have to be adopted, which consider in much more detail the precise structure. The fundamental idea is not changed; namely, to find the energy of the lattice as a function of the lattice spacing. If one knows the lattice spacing at equilibrium at atmospheric pressure, and the energy at all spacings, one knows the difference of energy between the equilibrium spacing and some other. From this one can find at once the magnitude of the pressure necessary to increase the energy by this amount on compressing the lattice from the initial to the final spacing, and thus the volume as a function of pressure. At ordinary temperatures this calculation would have to be corrected for various temperature effects; these corrections are not easy to make, so that one is usually satisfied to calculate the compressibility at zero absolute, where the corrections vanish. This is usually good enough, because experiment shows that compressibility does not vary by a large amount with temperature.

The numerical working out of the energy as a function of volume has up to the present been carried out for only a few of the simplest cases. One can guess that a rigorous mathematical solution is of absolutely prohibitive difficulty. It is known that in classical mechanics the problem of three bodies moving under their mutual forces of gravitation has not been completely solved; here we have the problem of 10^{22} atomic nuclei per unit volume, each nucleus accompanied by from 2 to 92 electrons. Obviously the only hope is in making certain approximations. The nuclei are at once dealt with by assuming that they are stationary at the points of the lattice; this practically means that the calculations are made for 0° Abs. The electrons are now to be dealt with by the equations of wave mechanics; into these equations enter the forces arising from the nuclei, and these forces are calculated from the positions of the centers of the nuclei by the old classical methods. That is, the nuclei are themselves not considered subject to wave mechanical treatment; in a general way the justification for this is that they are so much heavier than the electrons. The rigorous solution of the wave equations for even the electrons alone would be impossible. Rigorously, all the electrons should be treated together, each electron affecting every other. But fortunately this interaction is only slight on the average for pieces of material of ordinary size. This is shown by the fact that metals have specific properties—the density or the specific resistance determined from measurements on a piece containing 2 c.c. is the same, within experimental error, as that determined on a piece of 1 c.c. Corresponding to this, it proves possible in the first place to assign the vast majority of electrons to comparatively fixed positions near the individual nuclei, corresponding to the inner shells of isolated atoms. In general, the mutual interaction of these inner shells can be neglected except for the shells of contiguous atoms, when there is effectively a repulsive force opposing the penetration of a shell of one atom by that of another, as would be expected on purely intuitive grounds. This obviously permits an enormous simplification in the calculations.

The electrons that remain after this approximation are the outer or so-called valence electrons. These also can be handled approximately, but by a sort of approximation opposite from that applicable to the inner electrons. The periodic structure of the entire lattice enters essentially into the solution of the wave equation for these electrons; these electrons are the possession of the entire lattice and cannot be associated with any particular atom. As might be expected, the practical difficulties of working out the solution for these electrons depend on their number. It has been found possible to carry through the solution to a satisfactory conclusion for the simplest cases, that of the alkali metals, which have only one valence electron per atom, and in which the cores of the atoms are so small that the mutual interference of the cores of neighboring atoms can be mostly neglected. Other metals with only one valence electron per atom, such as copper, silver, and gold, can also be treated with some degree of success, but here the difficulties become greater because there is interference between the closed shells. If there are two outer electrons per atom, the difficulties become greater, and not so many of the properties have been subjected to successful calculation. It is perhaps unfortunate that theory is not yet in a position to make such successful calculations for most of the metals of industrial and technical importance.

The solution of the wave equation for the outer electrons for the alkali metals corresponds to a distribution of electrons throughout the lattice which is nearly uniform except in the immediate neighborhood of the nuclei. It follows that to a first approximation an alkali metal can be regarded as positive point charges arranged at the points of the lattice, embedded in a uniform sea of negative electricity. The electrons distribute themselves so that on the average they occupy all parts of space uniformly, owing to the mutual repulsion between them. This means that on the average the immediate vicinity of each nucleus is occupied by only one electron at a time. From this is derived an approximate method of calculation originally due to Wigner and Seitz. In the space lattice imagine lines drawn from every nucleus to its nearest neighbors in all directions, and imagine planes erected perpendicular to these lines at their middle points. The whole lattice is in this way divided into polyhedra. The approximation consists in treating each polyhedron as containing a single positive charge at its center, surrounded by a uniform sea of negative electricity of such density that the total negative charge in the polyhedron is also one unit, so that the polyhedron as a whole is electrically neutral, and accordingly exerts very little field at outside points. It follows that the energy of the system can be found to a good approximation by neglecting the interaction of the polyhedra on each other, and merely summing the energies of the individual polyhedra. The energy of a single polyhedron is composed of the potential energy of the electron cloud, plus the kinetic energy of the electrons. In calculating these energies, a further approximation is made by replacing the polyhedra by spheres of equal volume. When the volume of the lattice is decreased by the application of pressure, the two contributions to the energy change also. The potential energy consists of two parts: the energy of the negative cloud in the presence of the nucleus, and the mutual energy of the cloud on itself. It is easy to see that both these parts vary inversely as the linear dimensions; that is, as $v^{-1/3}$, assuming that when the lattice is compressed the cloud is compressed in the same ratio. The way in which the kinetic energy of the electrons varies with the dimensions of the lattice can be anticipated from the fundamental relation connecting the equivalent wave length of a free electron with its momentum, $p = h/\lambda$. That is, the momentum varies inversely as the wave length, and therefore the kinetic energy varies inversely as the square of the wave length.

In a block of metal the solution of the wave equation for the electron is a series of standing waves, the length of these waves being determined by the requirement that they shall fit without remainder into the dimensions of the block. If the block is changed in dimensions by pressure or otherwise, the wave length of each of the waves must change proportionally in order to maintain its fit. This means that the momentum of the electrons increases proportionally to the decrease of linear dimensions of the lattice, and the kinetic energy increases proportionally to the square of the decrease of linear dimensions, or proportionally to $v^{-2/3}$. The signs of the two terms $v^{-1/3}$ and $v^{-2/3}$ are opposite, potential energy being negative and kinetic positive. At large distances of separation of the nuclei one term preponderates, and at small distances the other. The two together give a curve for the energy which passes through a minimum. The position of this minimum determines the lattice spacing, and the variation of energy in the neighborhood of the minimum the compressibility. It turns out that rather good values for the lattice constant and for the initial compressibility can be obtained for the alkali metals by

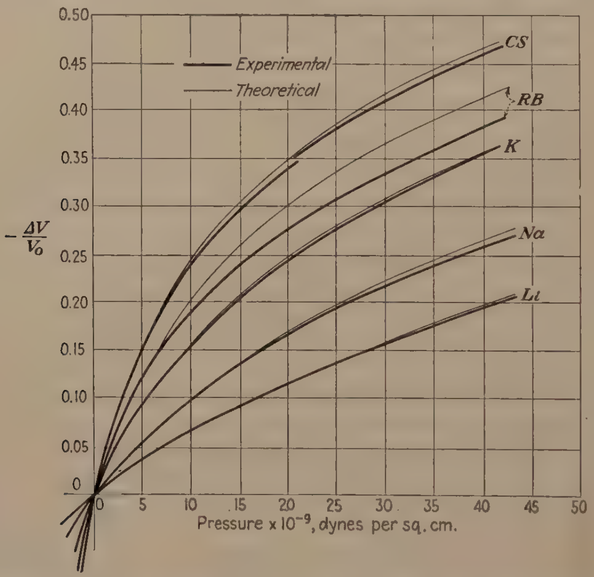

Fig. 4.—Experimental compressions of alkali metals compared with results calculated theoretically by Dr. John Bardeen.

this simple picture. However, for the other metals with one valence electron—copper, silver and gold—the agreement is not nearly so good. The explanation has been sought in the fact that the ion cores for these metals are much larger than for the alkalies, so that there are mutual repulsive effects due to relative impenetrability of the ions. These forces must also be active to a lesser extent with the alkalies. Calculations show that this force would be expected to vary inversely as the volume. Putting all three terms together, the energy of the metal would be expected to have the form:

$$W = a/v + b/v^{2/3} - c/v^{1/3}$$

With a formula of this type, Dr. Bardeen has reproduced the volume of the five alkali metals with a gratifying degree of approximation up to the limit of the experimental range. In Fig. 4 are shown the theoretical and experimental curves. It turns out that by far the most important term is the increase of kinetic energy of the electrons when the lattice is compressed. The other metals, however, have up to the present not been so successfully dealt with.

3. Resistance at High Pressures

We now turn to the third group of phenomena, the resistance of metals at high pressures. As already stated, the apparatus necessary for measuring resistance is larger and more complicated than that for the other two effects, so that it has proved possible up to the present to make measurements only to 30,000 kg. per sq. cm. Previously measurements had been made to 12,000, and in a few cases to nearly 20,000. These previous measurements had shown that the resistance of most metals decreases under pressure, but at a rate which becomes less as pressure becomes higher. There are, however, a fair number of metals whose resistance increases under pressure, and for these, surprisingly, the rate of increase of resistance becomes greater as pressure increases. In addition, three examples had been found in which the resistance passes through a minimum with increasing pressure. In all cases, the plot of resistance against pressure is convex toward the pressure axis. In general the changes of resistance are greater for the softer metals with low melting points. Furthermore, the order of magnitude of the changes of resistance with pressure is 10 times greater than that of the corresponding change of volume.

In the new range, measurements were made first on some of the high-melting metals: copper, silver, gold and iron. The effects here are about what might be expected—smooth continuation of the results previously found at lower pressures. The plot of resistance against pressure continues convex toward the pressure axis, but any eventual minimum is so far away as to discourage extrapolation. The softer metals give more interesting results. One might expect the effects with the alkali metals to be large, and easiest for the theoretical physicist to handle. Lithium is different from the other alkalies in that its resistance increases with pressure from the very first. Up to 30,000 kg. per sq. cm., the increase continues at a continually accelerated pace, until at 30,000 the resistance is nearly 25 per cent greater than initially. The resistance of sodium, on the other hand, decreases rapidly, but with upward curvature. The resistance at 30,000 is about 0.4 of its initial value. Potassium is softer and more compressible, so that the effects with it might be expected to be larger. This in fact proves to be so, and the resistance of potassium at 30,000 is less than 0.2 its initial value. But the most interesting feature of potassium is that the resistance passes through a minimum in the neighborhood of 25,000; this had been anticipated from previous measurements, but sufficient pressure had not been available at that time actually to realize the minimum. Rubidium at first decreases in resistance more rapidly than potassium, but then passes through a minimum in the neighborhood of 16,000, as had already been found.

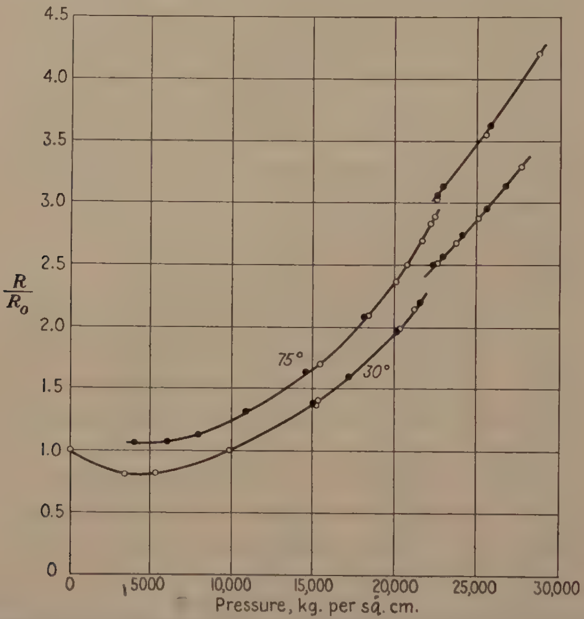

Fig. 5.—Resistance of caesium at two different temperatures as function of pressure. Break in curves corresponds to polymorphic transition.

In the new pressure range resistance continues to increase, and at a constantly accelerated rate. Caesium had been previously found to have a minimum in the neighborhood of 5000, and above this the resistance became rapidly larger. One of the most interesting results to be anticipated in the new range was with regard to the new polymorphic modification of caesium formed at 22,000. The new high-pressure modification has, of course, a smaller volume than the low-pressure modification, so that it would be expected in the first place that the resistance would decrease on passing to the new modification, since in all known examples of phase change the resistance follows the change of volume. In the second place, one might anticipate that the resistance of the new modification would decrease under pressure, since it is only the unusual metal whose resistance increases under pressure. Both these anticipations proved to be exactly wrong; the resistance increases on passing to the high-pressure phase with its smaller volume, and the resistance of the new phase continues to increase with increasing pressure. In Fig. 5 is shown the resistance of caesium as a function of pressure. In general not much disturbance in the resistance is produced by the change of phase, the curve continuing through the phase change without any marked alteration in its character.

The alkali earth metals might also be expected to show large effects. The resistance of calcium and strontium was already known to increase with pressure—in the new range it continues to increase at a continuously accelerated rate. At 30,000 the resistance of strontium has grown to nearly 3.5 times its initial value, the largest increase of resistance measured for any substance. Barium had been previously found to pass through a flat minimum of resistance and then to increase. The question of interest here was the same as with regard to caesium; namely, how will the new high-pressure modification behave? The resistance proves in the first place to decrease slightly on passing to the high-pressure modification, thus obeying the rule with respect to volume to which the only exception thus far is caesium; but, on the other hand, the curve of resistance continues to rise beyond the transition, and the general effect of the transition on the resistance is only slight, as was also true for caesium.

Mercury is a low-melting metal and fairly large effects might be expected. The freezing temperature of mercury is raised by 30,000 kg. per sq. cm. to above 100° C., so that in this range it is easy to make measurements on solid mercury. It turns out that the resistance of mercury decreases under pressure at a rate about 50 per cent greater than does that of lead, a result which feels reasonable enough.

Interesting results are to be anticipated from the measurement of the effect of pressure on the resistance in different directions of large single crystals of the noncubic metals. Zinc decreases in resistance in all directions, but there is a curious dissymmetry of the pressure effects in different directions, so that at high pressures the relative resistances along the principal crystallographic axes are reversed. Single-crystal tin decreases smoothly in resistance over the entire pressure range and in all directions, and shows no reversals. Single-crystal antimony is the only example of a metal whose resistance at first increases with pressure but then passes through a maximum and then decreases; this anomaly holds only for certain directions. Tellurium is interesting because it is only semimetallic in its properties. It was already known that the resistance decreases enormously with increasing pressure. Measurements in two different directions of the crystal show that in the extended pressure range the resistance continues to decrease rapidly, until at 30,000 the resistance is only $\frac{1}{600}$ of its initial value. There is not much difference between different directions in the crystal. The most interesting feature of the behavior of tellurium is with regard to its temperature coefficient. The resistance of all true metals increases with rising temperature, but tellurium betrays its nonmetallic character by a negative temperature coefficient of resistance. However, at high pressures, the temperature coefficient is found to reverse sign, becoming positive like the true metals, so that with a certain justification one may say that the effect of pressure on tellurium is to squeeze it more nearly into the state of a metal.

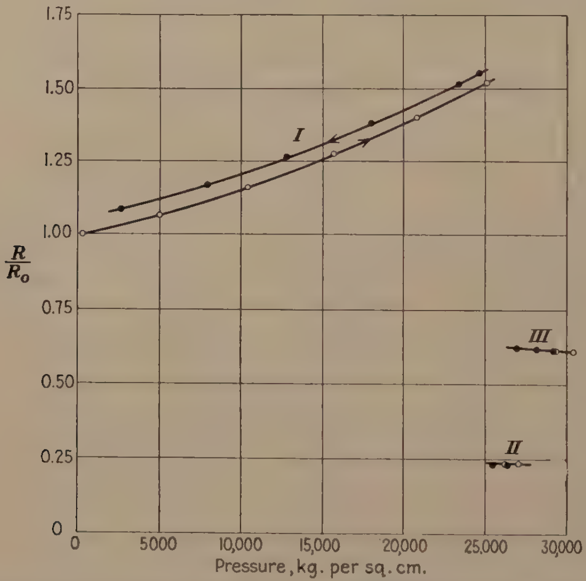

FIG. 6.—RESISTANCE OF BISMUTH AT 30° C. AS FUNCTION OF PRESSURE UP TO 30,000 KG. PER SQUARE CENTIMETER.

Different segments represent resistance of different polymorphic modifications.

Finally, bismuth would be expected to be of interest because of its two transitions in the range up to 30,000. Ordinarily bismuth is abnormal in that its resistance increases with pressure. The resistance is now found to increase in the new pressure range up to the first transition point, shown in Fig. 6. Here the resistance *drops*, as is to be expected because of the direction of volume change, and by a factor of 6, which is unusually large. The new high-pressure modification is now found to decrease in resistance with increasing pressure, the first time that this expectation has been fulfilled. But now at the second transition point, the resistance *jumps up* again, in opposition to the change of volume and by a factor of 2.6. In this respect bismuth III (or perhaps rather bismuth II) is abnormal, but on the other hand, bismuth III, like bismuth II, has a negative pressure coefficient of resistance.

The experimental situation in this new pressure range is thus somewhat complex; in the present state of theory one could reasonably expect that only the simplest features of the experimental situation could be reproduced. Even the theory which can deal with the simplest effects has to be much more complicated than the theory which was sufficiently good to give energies, lattice constants, and compressibilities. It is not possible in this lecture to attempt to give a complete account of the wave-mechanics theory of electrical resistance; only the principal points can be suggested. It is in the first place to be considered that the electrons are not distributed over all velocities. The entire block of metal is to be regarded as in a certain sense a gigantic molecule, and there will be structure in the way in which the electrons are arranged in it, analogous to the structure with which electrons are arranged in shells in single atoms. In fact, one can get an idea of the nature of the energy structure of the electrons in the whole metal by imagining the metal assembled from the individual atoms at infinite dispersion, the shells in the individual atoms passing continuously into energy bands of closely packed energy levels in the assembled metal. Just as in the isolated atoms there is a structure for the energy which the electrons may acquire under external stimulation, as well as for the energy they possess when undisturbed, so in the metal there is a structure of the energy states to which the electrons may be excited as well as a structure for the energy states which they assume when undisturbed. The "zone" theory of metals is the theory which takes account of the energy structure of the electrons, and it is the properties of the zones which are primarily concerned in phenomena of electrical resistance.

Under ordinary conditions the energy the electrons have in virtue of their wave character is much greater than the energy they would have because of temperature agitation. At 0° Abs. the electrons all settle down into the lowest possible energy states, filling all these states full, with unoccupied states of higher energy above them. When temperature increases, it is only a few of the electrons, near the top of the occupied energy states, which can acquire sufficient energy from the bombardment of the atoms to be raised to those higher energies which are permitted to them by the energy structure. This is the explanation of the fact that the electrons make a very much smaller contribution to the specific heat than would have been supposed by classical theory; the explanation of this fact was the first great striking success of the new point of view in explaining the properties of metals. Similarly, when an external electric field is applied to the metal, the electrons can acquire energy from the field—that is, move under the influence of the field so as to constitute a current—only when there are unoccupied states in the energy structure to which the electrons may move. According to the nature of the energy structure, we may have different sorts of behavior of the electrical resistance. It may happen that the topmost band in the energy structure which is occupied by electrons at all is only half filled by electrons; this is true of the alkali metals, which have only one valence electron per atom. In such metals there are unoccupied energy levels close at hand to each electron, to which it may be easily excited by an external field, so that the electrons in such metals respond readily to external fields, and the metal is a good conductor. The metal is not an infinitely good conductor because of continual dissipation of the energy absorbed by the electrons from the field by collisions with the atoms, which are moving irregularly because of temperature agitation. On the other hand, if the atoms each have two valence electrons, the uppermost occupied energy band is filled completely with electrons in their natural unexcited state. The only way in which the electrons of such a substance can acquire energy from an external field is to be advanced to positions in other unoccupied energy bands. If the next unoccupied energy band is some distance above the occupied band, the electron will not be able to acquire sufficient energy from the field to make the jump, and the material will be an insulator. This is the state of affairs with many nonconductors. If on the other hand, the next band is very close to the occupied band, or actually overlaps it, it will be easy for the topmost electrons to be excited by the field, and the material will be a conductor. This is the case with the bivalent alkali earth metals.

When a material is compressed, the energy structure is going to be altered, and the resistance will be altered. In the detailed working out of the effects, several factors will have to be considered. The rate at which the energy acquired from the field is dissipated to the atoms is affected by pressure. Here it proves that analysis made before the advent of wave mechanics gives approximately the correct answer; the rate of dissipation is proportional to the square of the amplitude of atomic vibration. As pressure increases, the natural frequency of vibration of the atoms increases because of the greater intensity of the restoring forces at small volumes, and the amplitude decreases. This factor would therefore produce a decrease in the resistance with increasing pressure. This is probably the most important effect with most normal metals, and it is for this reason that the resistance of most metals decreases under pressure. There is another important effect. It is to be expected that the old picture of a free electron would not correspond exactly to the situation in wave mechanics. It turns out that if the electron is situated in the middle of an energy band the old picture is good enough, and the electron can be thought of as having its normal mass, and its kinetic energy is the square of its momentum divided by twice its mass. But near the top of an energy band this simple relation between momentum and energy ceases to hold. Here for a time the energy does not change, although the momentum may be changing, and then there is a sudden snapping of energy to a higher value with no change in momentum. In this region the electron is not "free," as it is in the center of the band. The average behavior of the electrons in the band will be a sort of mean between that of those free and those not free; in other words, the "effective" number of free electrons will be less than the total number. The ratio of the "effective" number to the total number will depend on the detailed structure of the band. This will in turn depend on the pressure, so that we have the possibility of an effect of pressure on resistance which was not contemplated in classical theory; namely, an effect on the "effective" number of free electrons. Detailed calculation shows that this number may either increase or decrease with pressure, so that we have here a mechanism which may explain the increase of resistance with pressure observed in some metals.

There is still a third factor, arising from interaction between the ions, which has been taken into account by Dr. Bardeen. It appears that this factor also may either increase or decrease with pressure. The detailed calculations of the relative magnitudes of these effects in any special case are difficult, but they cannot be avoided, because it is not possible to see intuitively whether the number of free electrons, for example, should increase or decrease with pressure for any special metal. Dr. Bardeen and Mr. Weiner have carried through the calculations for lithium and sodium, taking account of the variation of all three factors. For lithium it turns out that there is a decrease in the number of effectively free electrons with increasing pressure more than sufficient to overbalance the other factors, so that there would be expected to be a net increase of resistance with pressure, as is the experimental fact. The numerical agreement is not good, however. For sodium, on the other hand, detailed calculation shows that practically the entire effect arises from the change of amplitude of atomic vibration, and it is possible to compute the resistance with good approximation over the entire range of pressure.

When more powerful methods of calculation are developed it will be possible to extend the calculations to other metals. In the meantime there is no reason to think that the fundamental equations are not capable of dealing with the situation, and that the difficulties are not entirely practical ones due to the difficulty of the calculations. One of the jobs which most obviously lies ahead of theory is to extend its calculations to single crystals in order to give some account of the variation of mechanical and electrical properties in different directions; this, theory has as yet hardly attempted.

THEORETICAL STRUCTURE

In conclusion, I want to comment briefly on the character of the theoretical structure that is growing up. It is yet too early to expect that the practical man can use theory as a tool with confidence that it will give him insight into new situations. It is true that many features of the new theory can be talked about in the easy intuitive way that made our old mechanical models so valuable, but I think if one examines the situation he will find that the intuition which is successful is a highly sophisticated intuition, and that without a previous detailed mathematical analysis by someone, intuition could not be safely followed. Thus we have come to talk intuitively of energy bands populated by electrons, and have learned how to use this picture to make many results appear plausible. But this picture cannot be handled with the thoroughgoing naïveté with which we could handle our old mechanical models. Thus we may not ask: "Which are the particular electrons in the energy band which have the lowest energies, or in which part of the metal are they situated?" This question makes no sense from the point of view of wave mechanics, although the natural implications of language make it a very natural question to ask. The intuitions which the theoretical physicist is developing to meet these new situations are intuitions based only partly on our previous experience, and in any new case the proper intuition has to be found and developed by the difficult method of detailed mathematical analysis. In these early days of this new subject those of us who are not primarily theorists can only sit and be instructed by those who have tediously worked through the details.

Production and Some Testing Methods of Metal Powders

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(New York Meeting, February, 1938)

It is, of course, expected that manufacture of the various metal powders should involve numerous methods adapted to the specific characteristics of the metals themselves. Several methods for powdering a particular metal may be available, but the physical characteristics of the powder as produced by the several methods may be quite different. In the final analysis, the application of the metal powder dictates the physical properties that the metal powder must possess, and this, to a very large extent, will determine which of several possible methods of manufacture is adopted. Sometimes powder of the same metal is produced by more than one method, each powder having specific characteristics that make it particularly suitable for its application.

For purposes of classification, the various methods of powdering metals can be grouped as follows:

1. Machining.
2. Milling (by ball mills, stamps, attrition mills, etc.).
3. Shotting (pouring molten metal into water, air, etc.).
4. Granulation (by stirring molten metal while solidifying).
5. Atomizing (disintegrating by steam, compressed air, etc.).
6. Condensation of metal vapor.
7. Reduction of oxide powders.
8. Chemical precipitation.
9. Electrolytic deposition.
10. Sintering (for producing alloy powders).
11. Formation of an alloy followed by dissolving or otherwise removing one of the alloying constituents.

MACHINING

Turnings, cuttings, filings, etc., are, of course, produced as by-products in machine work of various kinds, and find certain applications as metal powders. For example, iron powder so produced is used extensively as a reducing or precipitating agent and as a constituent in certain hard-finish cements.

Manuscript received at the office of the Institute Dec. 1, 1937.

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In general, these products are rather irregular in particle shape and relatively coarse, although fairly fine powders can be obtained by filing operations. The various machining operations may be used, of course, with the direct object of producing metal powders when particular powders are not obtainable as by-products. When relatively coarse powders are required, this type of operation is used occasionally, although production rates are necessarily low per machine and the cost correspondingly high.

Certain expensive alloy powders, such as those used in the dental trade, may be produced in this manner. The quantity of the alloy produced is not so great as to make this rather crude method impractical from a cost standpoint, particularly since the rather excessive cost of the operation is not too great in relation to the cost of the alloy itself. Freedom of the powders so produced from extreme fines or "slimes" is also an important consideration for some powder applications and is partly responsible for the selection of this type of process for manufacture of dental alloy powders.

This general type of powdering process needs no detailed consideration here, as the exact machining operation used depends entirely on the ingenuity of the operator in adapting commonly known machining operations to produce in the most efficient manner the size and shape of metallic particles required.

Milling

Stamp mills, ball mills and various types of attrition mills are used for production of numerous metal powders.

Milling of friable metals or alloys presents no particular problem. For example, metals such as antimony, bismuth or silicon, and brittle alloys such as certain copper-aluminum, aluminum-magnesium, copper-tin, nickel-iron, nickel-zirconium, nickel-copper and phosphor-copper, can be ground to powder in ball or attrition mills. A preliminary crushing or "shotting" operation may be necessary to break these metals down to a size that can be conveniently handled by the grinder used for the finishing operation. Heavy stamps, jaw crushers or gyratories are suitable for such preliminary crushing treatment.

Some of the harder metals, such as chromium, manganese, molybdenum, nickel and titanium, can be pulverized in ball or attrition mills. In general, these harder metals must be broken down to a finer stage in the preliminary crushing or "shotting" operation and the wearing parts of the mill used for final grinding must be of some hard composition to resist abrasion from metal powders. Also, since a considerable amount of heat is developed in the grinding operations, it is sometimes necessary to provide means of keeping the metal cool during working, to avoid "smearing" of the powder on the grinding surfaces, which would occur if the metal were allowed to reach a temperature at which it is malleable. Milling of malleable metals presents a somewhat different problem and requires special treatment.

A stamping or hammering process is generally used for producing such powders, the resulting powder being flaky.

In order to prevent "welding" together of the metal powders under impact and to facilitate their flowing out and breaking up into thin flakes, a lubricant is usually employed to coat the surfaces of the powder during milling.

As a preliminary step, the metal is melted and splashed into water, atomized, or otherwise broken down to a feed size for the mills used in the flaking operation.

The flaking operation may be carried out in stamp mills, or in ball mills if the type and intensity of milling action is carefully controlled.

Where stamps are used,[1,2] it is customary to perform the initial flaking in relatively heavy stamps, the product then being transferred to lighter stamps better adapted to finer flaking. Depending on the character of the metal and the fineness of the product desired, the stamping may be completed in the second set of stamps or may be finished in a third, still lighter, set.

In the Hametag process,[3] the metal is flaked out in a ball mill. Together with a small amount of lubricant, the metal is continuously fed into one end of the mill and a current of inert gas sweeping through the mill carries the flakes out of the mill into a classifier as they approach the desired degree of fineness, the oversize flakes being returned to the mill for further treatment. An inert gas is used to prevent excessive oxidation of the metal during flaking and, with aluminum, to prevent explosion, as aluminum in finely divided form suspended in air presents a definitely dangerous explosion hazard.

The Hall process[4] also makes use of a ball mill, the metal to be flaked being charged into the mill together with a solution of the lubricant in an organic solvent, the mixture forming a sludge. After flaking, the solvent is removed by distillation. In this process, since the metal is "wetted" down during flaking, no dust explosion hazard exists.

Metals dangerous to handle because of a dust explosion hazard, such as magnesium, may be safely powdered by either of these two ball-mill processes.

Aluminum, copper, lead, iron, nickel, magnesium, copper-base alloys, Monel metal and German silver are examples of powders that can be produced by these flaking methods. The products, being, in general, flaky and of low apparent density, are not well suited to all types of applications but are very desirable for certain uses.

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[1] References are at the end of the paper.

Copper flake is used extensively in the manufacture of motor brushes for commutator and collector rings, being compounded with carbon or graphite and occasionally smaller amounts of lead or tin. The flake type of copper appears to have some advantage for this application, owing to its tendency to laminate during molding. By molding the brush from the side, the laminated layers run parallel to the electrical current when the brush is in use, resulting in improved electrical conductivity. Granular types of copper powder produced by methods described later have also been found advantageous for manufacture of certain types of motor brushes and are used in considerable quantities for this purpose.

Aluminum flake is used for pyrotechnical work, as in the manufacture of "sparklers," star shells, flares, and, to some extent, as a constituent in liquid-oxygen explosives. Aluminum flake is used in compounding certain types of hard rubber tires, where it aids in the curing of the rubber. As a constituent in aerated concrete, the aluminum reacts with a weak alkaline water solution in the concrete to generate hydrogen, which, when liberated during the setting of the concrete, blows the mixture full of gas bubbles and causes the mixture to set as a porous mass.

The most important use of flaked metal powders today is in paints. The flake structure of such powders provides an enormously greater unit surface than granular powders of the same mesh, and when these flakes are properly oriented in a paint film they provide an approximately continuous metal film, which makes the powder particularly effective as a paint pigment, from the standpoint of both serviceability and decoration.

In the manufacture of flake powders for use in paints, the production of a flaky powder is only one of the problems. To be effective as a paint pigment, these flakes must have the property of floating on the surface of the varnish or oil vehicle in which they are generally applied. This floating phenomenon is described in the paint trade as "leafing" and it is this "leafing" characteristic that permits flakes to arrange themselves at the surface of the paint film with their flat surfaces parallel to the surface of the paint film, forming the metallic coating characteristic of these metal paints.

Leafing characteristics are imparted to the flake powders produced in stamps or in the Hametag process by subjecting the flakes to a polishing action. The powder, together with a small amount of a polishing agent such as stearic acid, is charged into a cylindrical drum fitted with polishing brushes, which are caused to travel over the inner surface of the drum and polish the powder, at the same time working the polishing agent uniformly onto the surface of the flakes. After the polishing operation, the powder is allowed to "age" for a period varying from several weeks to several months, during which time the polishing agent becomes attached to the surface of the flakes in what is believed to be some definitely oriented manner. It is this definite film on the surface of the flakes that is responsible for leafing of the powder.

In the Hall process[5] an organic solution of a polishing agent, such as stearic acid, may be used to serve as both the lubricant during flaking and to develop the leafing characteristic of the powder simultaneously with the actual flaking, eliminating the necessity of subsequent polishing and aging. Since a paint or varnish thinner may be selected as the organic solvent, the product may be left in paste form by removal of excess solvent after flaking and the product marketed as a paste pigment to be incorporated with the usual paint vehicles. When the product is desired in powder form, the solvent may be removed completely by distillation.

Flake powders, after thorough degreasing and cleaning of their surfaces, can be treated with aniline dyes to produce various brilliant colors. The copper and copper-base alloy powders can be given heat-treatments under carefully controlled oxidizing conditions to bring out brilliant colors ranging from deep crimson to purple. None of these colors are absolutely light-fast and these powders do not possess leafing properties, but for certain applications they are quite satisfactory.

Flake powders used for certain decorative purposes, such as lithographing, and for coating paper from casein solutions, are not required to "leaf out," and for such applications a minimum of polishing agent is used in manufacture of the powder or, for application in casein, special polishing agents may be used to produce surface films that are more readily "wettable."

The Eddy mill[6] is another, somewhat novel, method being used today for disintegration of malleable metals. By this method, metal previously subdivided into relatively fine size (fine wire chopped into short lengths being used in one operation) is continuously or intermittently fed into the Eddy mill. Fans or impellers are so mounted in the machine as to cause opposing gas-eddy currents of sufficient velocity to pick up the metal particles and whirl them against each other with enough force to cause the particles to disintegrate when collision occurs. Since the impact is stated to occur between the metal particles only and not against the surfaces of the mill or impellers, contamination from wear on the mill is eliminated. The powder so produced is roughly spherical in shape and is suitable for molding applications. Since the apparatus can be designed to be gastight, an inert atmosphere may be employed when desirable. Relatively soft metals, such as iron and copper, have been successfully powdered in this apparatus.

SHOTTING

A relatively coarse and roughly spherical shot powder can be produced from metals, which do not oxidize too rapidly in air, by allowing molten metal to drop through a screen or through small orifices, solidifying in air and dropping into water. Metals subject to rapid oxidation in air may, of course, be "shotted" in an inert atmosphere by the same general method. The height of drop and size of orifice determine the size and shape of the particles. The water serves as a cooling medium and prevents agglomeration of the particles. Aluminum shot produced in this way is used almost exclusively for deoxidation of steel. Lead shot is formed by allowing the molten lead to drop through small orifices. A small percentage of antimony may be added to the molten lead, its addition increasing the surface tension of the molten drops falling through the orifices and causing them to become almost perfect spheres as they solidify in air before dropping into the water.

When the granulated product may be irregular in shape, the molten metal may be dropped directly into water, "feathered" zinc being made in this manner.

GRAINING

Certain metals, such as aluminum, cadmium and zinc, and alloys such as brass, break up into metal granules if stirred while solidifying from molten condition. This is commonly explained by the statement that the metal is "hot-short." It seems probable that stirring the metal in its "mushy" stage just before solidification incorporates air, which coats individual particles of the metal and prevents coalescence. Such powders are relatively coarse and high in oxide content, as compared, for example, to products obtained by atomizing. Aluminum powder so produced is used in the Thermit process. Granulated brass is used in certain brazing applications.

ATOMIZATION

Atomization essentially is the forcing of a thin stream of metal through a small orifice and hitting the stream of molten metal with steam or compressed air or gas, which disintegrates and solidifies the metal into finely divided particles of ragged "tear drop" shapes. In one application of this method, steam or compressed air that has been preheated to approximately the melting point of the metal is directed through a nozzle (partly submerged in the molten metal) in such a manner as to draw the metal up through a tip that is inside the nozzle. By proper design and arrangement of the nozzle and tip assembly, by adjustment of steam, air or gas pressure, and by varying the viscosity of the molten metal through control of the amount of superheat of the metal, the degree of fineness of the atomized product can be regulated over a considerable range. The atomized metal is carried off under suction to a dust-collection system such as a cyclone dust collector and baghouse. Steam or compressed air might be expected to result in excessive oxidation, but this does not occur because of the extremely rapid chilling effect of the expanding gases released through the nozzle. There is very little oxidation even of metals such as aluminum, zinc, tin or lead. These metals, when atomized with compressed air, contain less than 0.2 per cent oxygen as oxide. While an inert gas might be substituted for air or steam in this process to further reduce the possibility of oxidation, this precaution for most metals is not necessary, and if an inert gas is used, considerable care must be used to prevent spontaneous combustion when the metal powder is subsequently exposed to air. On the other hand, the thin film of oxide produced during atomization with steam or air is sufficient on aluminum, zinc or tin to prevent further oxidation of the powders. Lead powder, no matter how produced, slowly oxidizes when stored in air.

This method is applicable to metals or alloys having melting points up to about 700° C. Above these temperatures, excessive temperatures are required in the coils used for preheating the steam or compressed air, and the materials used for tips and nozzles rapidly deteriorate.

As always when finely divided explosive dusts such as aluminum and zinc are handled, it is important to eliminate all possibility of producing sparks in the dust suspension. The fans used to produce the suction required to remove the atomized dust are placed on the discharge side of the dust-collecting system, so that the fan operates in a dust-free atmosphere. The dust suspension must never be drawn through the fan, where a spark might be caused by the impeller striking a metal surface. All equipment must be thoroughly grounded to prevent a spark caused by static discharge.

It is possible to produce powders of a considerable range of fineness by the method just described, but for coarser powders that are required to contain a minimum of fines, and for atomization of metals having a melting point higher than about 700° C., the cross-jet method is better. In this a stream of molten metal is forced through an orifice, or is otherwise allowed to pour into a jet of steam or compressed air directed substantially at right angles to the stream of molten metal. Danger of dust explosions in this method is not so great as in making the finer grades by the first process considered, but the problem of dissipating the heat is greater, because of the slower cooling of the somewhat larger particles. A larger collecting system must be used.

Atomized tin, lead, zinc and aluminum are suitable for molding work of various kinds, and lead powder so produced is used in metallic packing and brake-band compositions. Atomized copper has not been found as well suited for molding work as copper powder produced from oxides or produced electrolytically. Molded products made from atomized copper are definitely lacking in mechanical strength. Zinc dust produced by atomization is used in the chemical industry as a reducing agent, and for sherardizing steel as a substitute for galvanizing. Atomized aluminum is used for pyrotechnics and for the calorizing process of protecting steel with a coating of aluminum. Recently a mixture of aluminum and copper with other chemicals has been developed which generates heat when moistened; in the form of pads this is used for the setting permanent waves in the hair-dressing industry without the use of electricity.

CONDENSATION OF METAL VAPOR

This process is well illustrated in the distillation of zinc dust. In the reduction of zinc oxide to zinc by the distillation process, zinc oxide is vaporized in a retort and reduced to zinc vapor by carbon monoxide. The carbon monoxide is generally produced by the burning of powdered coal, which is intimately mixed with the zinc oxide in the retort. The zinc vapor produced in the retort passes into condenser tubes where it condenses as molten zinc. In order to produce zinc that will coalesce to molten zinc in the condenser tubes, it is necessary to keep the carbon dioxide content of the gas in the system at an extremely low concentration.

In the early stages of the distillation cycle, the carbon in the charge will burn with production of an excessive amount of carbon dioxide, which, at the retort temperature, reacts with zinc vapor to form zinc oxide. When properly operated, the gas in the system will be held to a carbon dioxide content just sufficient to cause a thin coating of zinc oxide to form on the surface of the condensing zinc; however, this coating of zinc oxide prevents coalescence of the zinc particles and a finely divided zinc dust results.

Rapid cooling of the gas-zinc vapor mixture also tends to produce powder rather than molten zinc, and in the early stages of the distillation cycle the zinc vapor content in the gas and the relatively cool temperature of the condenser tubes tend toward rapid condensation with production of powder. Such powder is commonly referred to as "blue powder." In normal operations, a considerable amount of this blue powder is made as a by-product before the system is brought up to proper operating conditions for production of molten zinc, and this by-product powder is marketed as zinc dust. In the past, such by-product powder contained an excessive amount of oxide as compared to zinc powder made by atomization.

By controlling excessive reoxidation in the early stages of distillation, or by diverting such powder, and collecting it separately from the product produced later in the cycle; by running the condensers at lower temperatures, and sometimes attaching what amounts to a second condenser (known as a "prolong") to the primary condenser, the powder can be rapidly condensed and will solidify in powder form. This powder, through control of the combustion gases, will contain a minimum of oxide film just sufficient to prevent coalescence of the powder, and will closely approximate the atomized product in freedom from oxide.

Powder of a particle size considerable finer than that produced by atomization can be so produced, and at a cost not materially higher than the cost of producing zinc in slab form. This type of powder is commonly used, together with zinc oxide, as a paint pigment. It is also desirable as a precipitant and reducing agent in numerous hydrometallurgical and chemical processes, where its characteristic fineness permits rapid solubility. The distillation process is not well adapted to the preparation of relatively coarse grades of zinc powder.

Carbonyl Process

The carbonyl process may be considered as a somewhat special application of this metal-condensation principle. In this process, as applied to manufacture of iron and nickel powder, the metal carbonyls are decomposed, giving metallic iron or nickel powder, and carbon monoxide. The oxide of the metal can be reduced to metallic state in hydrogen or water gas. If the reduced metal is then cooled to approximately room temperature and carbon monoxide passed over the metal, the carbonyl is formed. Nickel carbonyl is a gas at room temperature; iron carbonyl is a liquid at room temperature and a gas at about 103° C. Both carbonyls decompose to the metal and carbon monoxide at higher temperatures.

In production of carbonyl shot, the carbonyl gas is led into a heated chamber, where it decomposes and the metal is allowed to condense out on undersize shot obtained from a previous batch. The condensed metal builds up in layers on this finer shot, producing an "onionlike" structure. When the size of the shot has built up to the desired diameter, it is removed, the undersize being screened out and returned to the heated decomposing chamber to serve as nucleuses for further deposition.

If a fine powder is desired, the carbonyl gas is led into a heated chamber that is large enough to prevent deposition on the walls. In one patented operation, the walls of this decomposing chamber are cooled to prevent decomposition on them. Powder so produced is in the form of extremely fine, almost perfect, spheres, it being claimed that the particles are single crystals, although it appears more probable that the individual particles have the same "onionlike" structure as the shot. The powder or shot is extremely pure, containing practically no impurities other than a small amount of carbon and oxygen.

These powders find use in manufacture of magnetic cores and are used for other similar applications where an extremely pure powder is required.

Reduction of Compounds of the Metals

Several metal powders can be reduced from chemical compounds of the metal by treatment in reducing atmospheres at temperatures below the melting point of either the compound or metal. The oxide of the metal is the compound most commonly used in this process. Tungsten is probably the best known application of this method. Other metal powders commonly reduced from their oxides are molybdenum, iron, cobalt, nickel, and copper.

Since tungsten has the highest melting point of all known metals (3350° C.) reduction from its oxide at a temperature below its melting point is the method commonly used for obtaining the metal. Subsequent working of the metal powder into the form of extremely fine filament wires having tensile strength up to greater than 500,000 lb. per sq. in. is probably the classical illustration of powder metallurgy.

The metal tungsten is reduced from its oxide in a hydrogen atmosphere at a temperature of about 1000° C. Zay Jeffries has described details of the manufacture of tungsten powder,[7] the process for subsequently sintering and working the powder to form wrought tungsten products and the metallographic principles involved.

Powders reduced from their oxides have a granular spherical shape and a spongelike structure that makes them particularly adaptable for molding work. Some metals are directly available in their oxide form, as iron in the form of magnetite, or copper in the form of oxide scale from wire-drawing or sheet-forming operations. Purer oxides are generally obtained by chemical precipitation, by roasting of compounds of the metal, or roasting of a finely divided form of the metal itself.

Being relatively brittle, these oxides may be ground in ball or attrition mills to the required degree of fineness and are generally screened or otherwise classified before reduction, to give a product having the most desirable distribution of particle size. Reduction may be carried out in a hydrogen, carbon monoxide or other reducing gas mixture. The reduced metal, depending on the temperature of reduction, will be more or less firmly "knit" together into a "cake." This cake can be broken down to powder in various types of attrition mills. The properties of the finished powder are largely influenced by the oxygen content and particle-size distribution of the oxide, by the temperature of reduction, by the type of reducing gas employed, by the type of grinding used in breaking up the metal "cake" and by the particle-size distribution of the finished powder.

Sometimes more than one oxide of a metal is obtainable and powder reduced from the different oxides differs somewhat in physical characteristics. By blending various degrees of fineness of the two oxides in different proportions, it is possible to obtain powders having different properties, suited to different applications. This type of powder is principally used in the manufacture of molded products.

Chemical Precipitation

The deposition of one metal from a solution by another metal, depending on their positions in the electromotive series, has been common knowledge to chemists and has been utilized in preparation of metal powders both directly and in by-product recovery processes. For example, tin powder is produced from stannous chloride solution by precipitating with zinc. This powder is extremely fine, being used principally in coating paper and for molding work.

Silver is recovered from sweepings and waste plating solution by converting the silver to silver nitrate and precipitating with zinc or copper. Some silver powder made by this method has been used for making molded electrical contacts.

Copper is recovered from waste liquors and washings in smelting and refining plants by precipitating with scrap iron, but the resultant "cement" copper is usually so contaminated with impurities that it is returned to the smelting furnace.

In some hydrometallurgical applications, metals are precipitated out in powder form and can be treated to obtain the metals in a form suitable for powder applications. For example, in treatment of copper-refinery sludges, selenium and tellurium can be obtained as by-products by adding the flue dust from the sludge roasters (which contains both metals) to the hot water solution of the soda-niter slag from the doré furnaces. This hot water solution is neutralized with sulphuric acid, which precipitates the tellurium as oxide. The remaining solution is acidified with sulphuric and hydrochloric acids and sulphur dioxide passed through the solution to precipitate the selenium as a rust-red powder. By treatment with steam this powder is transformed to the black variety and can be ground in a ball mill. Selenium is used principally in photoelectric cells, because its electrical conductivity is greatly affected by changes in the intensity of light striking the metal. The red variety is also used to impart a ruby color to glass.

Tellurium is obtained from the oxide by fusing with powdered coal; the fused metal, being brittle, can be ground in a ball mill to obtain a powder. Tellurium finds some use as an alloying agent. In lead it replaces antimony as a hardening agent and increases acid resistance.

Electrolytic Deposition

In the numerous processes used for electrolytic refining of metals, the physical character of the metallic deposit may be varied with the composition of electrolyte used, temperature of the electrolyte, current density, rate of circulation of the electrolyte and by employment of certain addition agents. By proper choice of electrolyte and regulation of these various factors, it is possible to obtain a number of metals in powder form and in varying degrees of fineness and particle shape. Dr. Joseph Rossman[8] has abstracted the patent literature on this general method of producing metal powders.

In electrolytic production of metal powders, it is customary to use relatively high cathode current densities as compared to electrolytic refining practice. The high cathode current density produces a loosely adherent, spongy deposit on the cathode, which may be periodically removed by various means, such as scraping and "rapping" devices, and to a certain extent by rapid circulation of the electrolyte past the surfaces of the cathodes.

In general, the acid electrolytes used for producing powders contain a relatively low concentration of the metal and a high concentration of acid as compared to electrolytes used for refining or plating. A relatively high cathode current density is generally employed. Under these conditions hydrogen is usually evolved at the cathode, which prevents the copper from being plated out as a solid deposit on the cathode and is responsible for the loosely adherent spongy formation. This deposit characteristically consists of finely divided metal crystals having a "fern-like" microscopic appearance.

It is important that the metal deposit on the cathode be removed at frequent intervals, because if it is allowed to build up the surface area of the cathode is thereby increased and the cathode current density lowered to such an extent that the deposit becomes too coarse and tends to plate out. In order to ensure uniformity of particle size of the deposit, it is, of course, also necessary to carefully control the temperature and composition of the electrolyte and to provide adequate circulation of electrolyte. The latter precaution will also prevent excessive voltage drop by checking polarization.

By changing the composition and temperature of the electrolyte, and particularly by varying the cathode current density, the fineness of the powder produced can be varied over a considerable range. For some metals, it may be advantageous to use a cathode current density somewhat higher than the anode current density. Addition agents may also be used to improve the uniformity of the powder produced or to modify the type of deposit to meet specific requirements.

The deposited powder must be thoroughly washed to remove all electrolyte, as even small amounts of salts left with the dry powder will cause rapid oxidation when exposed to atmosphere. It is usually advisable, after thoroughly washing the powder, to dry the sludge in a vacuum or inert atmosphere, keeping the powder from contact with air until it has been thoroughly dried and cooled to approximately room temperature.

Some powders are heated in an inert or reducing atmosphere after drying, which has a tendency to improve the keeping (nonoxidizing) properties of the powder and tends to increase its apparent specific gravity by partial knitting together of the particles.

The structure of powder produced electrolytically is well adapted to molding work, although unless it is given a heat-treatment, as mentioned above, the apparent density of the powder may be too low for some applications. When produced under conditions resulting in a relatively high specific gravity, this powder behaves in practically the same manner as the "porous" type of copper powder made by reduction from oxide, and in many applications the two types of powder are used interchangeably.

Copper, zinc, iron, cadmium, tin, antimony, and silver powders are produced electrolytically, and as the art of electrolysis expands it may be expected that some of the more difficultly obtainable metal powders, such as tungsten, may be produced in this manner.

Several modifications and novelties in the application of the principals described above are mentioned in Dr. Rossman's abstracts. For example, one patent (Craig, British Patent 6161, year 1913) describes an electrolytic method of producing copper by using an electrolyte consisting of an acid solution of titanium and sulphuric acid. The electric current reduces the titanic salt to titanous condition at the cathode. Copper passes into solution at the copper anode and is reduced to a metallic powder precipitate by the titanous sulphate, and the titanic sulphate formed during precipitation of the copper is re-reduced at the cathode.

Several patents issued to Edison[9] describe a method whereby copper and nickel or cobalt are alternately plated out on a cathode, acid sulphate and ammonium sulphate solutions, respectively, being used as electrolytes. After a multitude of alternate layers of the metals is built up, the deposit is stripped from the cathode and cut into squares of the desired size. The copper is then dissolved out by a strong solution of potassium cyanide, leaving the nickel or cobalt in the form of thin flakes. The thickness of these flakes, of course, is determined by the thickness of the separate alternate layers plated out on the cathode between the alternate copper deposits.

SINTERING

It is possible to produce alloy metal powders by several of the methods described herein—by direct grinding of brittle alloys, machining, shotting, atomizing, and by codepositing of the metals electrolytically. Another method not considered earlier in this paper makes use of the property certain metals have of alloying below the melting point of the alloy formed. For example, copper and tin powders may be intimately mixed and heated in a neutral or reducing atmosphere at a temperature below the melting point of the alloy to be formed. As the melting point of tin is approached, it diffuses into the copper to form a bronze alloy, and as the temperature is then increased the tin and copper completely diffuse to form a uniform alloy of the composition represented by the proportions of tin and copper used. Since the temperature used is below the melting point of this alloy, the product is a sintered "cake," which may be ground to a powder with little difficulty. Where alloys are formed in this manner, from metals having such widely differing melting points as tin and copper, it is generally necessary to use a temperature above the melting point of the lower melting metal, in order to obtain complete diffusion of the metals within a reasonable time, and in this case the alloy cannot contain too large a percentage of the lower melting constituent; for example, a low-copper, high-tin alloy would fuse to a practically solid mass if the temperature of alloying were higher than the melting point of tin. Also, for some the temperature required for complete alloying is so high that the alloyed particles become knit into such a hard mass that it is almost impossible to grind the "cake" to a fine powder. When the alloying metals melt at close to the same temperature (as copper and silver) it is not necessary to use a temperature high enough to melt either of the metals or the alloy formed. If one of the constituents of the alloy to be formed is volatile at the sintering temperature to be used (as may be true of certain zinc-bearing alloys) it is necessary to provide an excess of this metal in the mix to compensate for volatilization loss.

By sintering mixtures of copper powder and red phosphorus, it is possible to produce copper-phosphorus alloys containing low percentages of phosphorus. These same alloys when cast cannot be conveniently pulverized. Certain phosphor bronze and brass powders can also be made by sintering.

Another interesting application of sintering is in producing so-called "master alloys," which are a dispersion of a high-melting-point metal, sometimes with partial alloying, in a strong matrix of copper. Such combinations can be added in the desired amount to a charge of molten metal when it is desired to incorporate small percentages of the high-melting-point metal. Combinations of copper and tungsten, copper and chromium, copper and molybdenum, or triple combinations like copper, nickel and molybdenum, as well as other combinations, can be sintered in the form of small disks or briquettes for such work.

Formation of an Alloy Followed by Removal of the Alloying Constituent

When metal powders are to be used as catalytic agents, they are frequently formed concurrently with the reaction they are to catalyze; however, the powder may be made up prior to its use as a catalyst, providing the metal powder is protected from the atmosphere during the storage period to ensure its being in an active state when used.

One of the methods used in preparation of finely divided and extremely active metal powders for catalytic work consists in alloying the metal with a second metal, which subsequently is dissolved out of the alloy. For example, aluminum can be alloyed with nickel and the aluminum dissolved from the alloy with caustic solution, leaving the nickel as a very fine, active powder.

Also, mercury can be used to amalgamate certain metals and the mercury distilled off, leaving the desired metal in a finely divided, active form.

Metal powders so produced are in fact so active as to be pyrophoric, and must be stored in an inert gas or in a suitable solution unless used directly as formed.

TESTING METHODS

The behavior of metal powders in their various applications and the physical properties of products made from metal powders depends to a large extent on the chemical and physical properties of the powders. It is desirable, of course, to have means of measuring or determining these various chemical and physical properties of the metal powders, and some such methods are outlined below.

Chemical analyses of metal powders are made by standard chemical methods, and need no further consideration here.

Such physical properties of molded products as strength, electrical conductivity, density or porosity, and growth or shrinkage of the product during heat-treatment, are a function of more than one characteristic of each powder ingredient. Satisfactory test methods for determination of each of these powder characteristics individually, by tests on the powder, have not as yet been worked out. As a means of determining the suitability of a powder for a definite application, test specimens may be molded and heat-treated, and the specimens may be tested to determine the strength and other characteristics of the powder under the specific treatment. Since these results are affected by the specific properties of all ingredients entering into the manufactured article, and by each detail of the molding and heat-treating operation, the data obtained on test specimens cannot always be correlated with production results unless specimens are made up exactly according to production procedure. At best such results are subject to the criticism of giving no definite measure of the individual characteristics of the powder responsible for the results obtained.

The apparent density of metal powders is important for several types of application. Density of a powder is determined by filling a cup of known volume with the powder, carefully leveling off the powder flush with the top of the cup and weighing the contents of the cup. The result can be expressed as weight per unit volume or as relative density (grams per cubic centimeter). In order to obtain consistent results, it is necessary to fill the cup by some uniform method; for instance, a Scott volumeter, which consists essentially of a series of glass baffles arranged to control the flow of powder so that it will be discharged into the density cup at a uniform rate.

Since powders used for certain types of molding work must flow into the molding dies readily, and since erratic flows will improperly fill the dies, a determination of the flow rate of powders is sometimes desirable. Powders can be tested for flow rate by determining the time required for a given weight or volume of the powder to flow through a standardized, funnel-shaped cup with a small orifice at the bottom. By allowing the powder from the funnel to fall into the density cup placed at a fixed distance below the discharge point of the flowmeter, a convenient and uniform method of filling the density cup is available.

Particle-size distribution of metal powders is generally determined by well-known screen-test methods. For most applications, such determinations are adequate to ascertain the suitability of the powder, and where successive lots of powder, made by a given method, are found to have practically the same percentages passing through a 325-mesh screen, the particle-size distribution of this subsieve fraction will generally be found to be substantially uniform.

For certain applications where slight variations in the particle-size distribution of the subsieve fraction has a marked effect in application of the powder, and particularly where the powder is so fine as to be practically all in the subsieve range, a determination of particle-size distribution below 325 mesh is desirable. A number of methods are available for such determinations. For general information on these and other methods, the papers by Lincoln T. Work,[10] and by Paul S. Roller[11] should be consulted, and for more specific details the reference cited on each particular method may be examined.

Subsieve sizes are usually expressed in terms of microns—a micron being equivalent to 0.001 millimeter. Various investigators have assigned values of from 45 to 60 microns as the average diameter of a particle just large enough to pass through a 325-mesh screen.[12,13] In using the following methods for metal powders, such a 325-mesh particle has been assigned a value of 50 microns, this value having checked out reasonably well with results obtained on metal powders by the several methods when correlated with screen-test data.

Microscopical Method

The microscopical method[10] for particle-size determination consists, essentially, of actually counting the number of particles in each of several arbitrarily established micron ranges by examining a slide of the powder through the microscope. For example, the number of particles between 0 and 5 microns in size appearing in a given microscopical field are counted and recorded. Similarly, the number of particles in each of the several other micron ranges are counted in the same microscopical field and recorded.

Only a very small sample of powder may be used on the microscope slide, making it important that this sample be truly representative, and that the powder on the slide be as uniformly dispersed as possible. As it is practically impossible to obtain absolutely uniform dispersion on the slide, a particle-size count of a rather large number of microscope fields on each slide must be made, and the composite results of the total number of fields added together. Where greater accuracy is desired, it is advisable to make a count of more than one slide to eliminate possible errors in sampling.

The particles on a slide may be measured by direct examination through the microscope, making use of standard grids in the eyepiece and estimating the particle sizes seen in the grid pattern. However, such a procedure is difficult and it is generally preferable to project the field onto a screen by means of a prism attachment on the eyepiece, so that the particles may be conveniently measured on the screen. Photographs may also be taken and the particles measured on the prints.

Measurement of irregular particles presents a problem. An average diameter may be estimated or the smaller diameter may be chosen, based on the assumption that such a diameter would determine whether or not the particle would pass through a screen having apertures equivalent to the given micron size.

An average size for all particles counted in each particular size range is assumed—for example, the average size for all particles in the 10 to 20-micron range would be assumed to be 15 microns. Then, from the total number of particles found in each of the several micron ranges, the percentage by weight of the powder appearing in each micron range can be calculated.

This method, if carefully carried out, is capable of giving fairly accurate and reproducible results, but is extremely time-consuming and tedious. For this reason, the method is not well adapted to control work and is of value principally as a research tool and as a direct method for standardizing other more rapid methods. This method is also subject to the criticism of using extremely small and, therefore, possibly not truly representative samples. Further, only two dimensions of a three-dimensional product can be seen. Measurement of the third dimension is almost impossible from a practical standpoint, making it necessary to assume the third dimension to be substantially the same as the dimensions measured.

The two other methods considered below depend in principle on the application of Stokes' law for falling particles, which, in general, states that where hindered settling is not encountered truly spherical particles will fall through a given gas or liquid medium at a rate proportional to the square of their diameters. In these methods it is assumed that the rate of fall of irregular particles is proportional to the square of their average diameters. Stokes' law stated by formula is:

$$V = \frac{2}{9} \times \frac{(P_p - P_1)g}{n} \times r^2$$

where V = velocity of fall,
P_p = density of particles,
P_1 = density of liquid,
n = viscosity of liquid,
g = gravity constant,
r = radius of particle.

Wagner Turbidimeter

In the Wagner turbidimeter,[14] the sample is dispersed in a suitable liquid medium having a viscosity that will allow the particles to have a falling rate suitable for taking the necessary readings entailed in the procedure.

The suspension is agitated to obtain uniform dispersion and then allowed to settle in a square-sided glass tank, placed in the path of a standard light beam, which strikes a photoelectric cell after passing through the suspension. The change in intensity of the light striking the photoelectric cell, as measured by a microammeter attached to the cell, is a measure of the change in turbidity of the suspension in the path of the light beam. Changes in the turbidity of the suspension are assumed to be in direct proportion to changes in the surface area of the suspension at any given level in the tank. It is possible, by application of Stokes' law, to calculate the time required for all particles of a given size to fall below the path of the light beam.

Microammeter readings are taken at predetermined time intervals arranged so that the difference between successive readings is a measure of the difference in turbidity due to removal of each successive particle-size range from the suspension at certain fixed tank levels.

These results can be calculated to give the relative proportions of surface present in each particle-size range, which in turn can be calculated to give the particle-size distribution by weight for the sample.

While for some materials this instrument can be calibrated on a theoretical basis by application of Stokes' law, for some metal powders determination of true density of the particles is practically impossible (as, for instance, porous powders resulting from oxide reduction) and it has, therefore, been necessary to calibrate this instrument for such metal powders by actually determining the falling rate of particles of the powder of known size in the particular liquid used for test. When this falling rate has been established, the falling rate of particles of all sizes of the same powder can be calculated by Stokes' law and the instrument calibrated for the particular powder as outlined above.

Although sufficient work has not been done with metal powders on the Wagner to permit an assumption that results are truly accurate in terms of particle size, application of this method has given results that check reasonably well with microscopical analyses and fairly reproducible results have been obtained. This method appears to be sensitive enough to clearly indicate any significant changes in particle-size distribution of metal powders. A complete analysis can be run in about 45 minutes.

Roller Air Analyzer

The Roller air analyzer[15,16] is also based on application of Stokes' law as applied to fall of particles through a rising current of gas. The powder sample is placed in the bottom of a glass U-tube, which is connected with a metal settling chamber of a known diameter. A jet of air is blown into the U-tube, the jet being adjusted in velocity to permit sufficient agitation to break up any agglomerates in the powder and to carry all the powder being separated out in the particular fraction, as well as part of the oversize powder, into the settling chamber. The volume of air forced through the jet is at first carefully adjusted and regulated to give a sufficient velocity of air passing upward through the settling chamber to carry over only the finest particles—for example, the 0 to 5-micron particles. These 0 to 5-micron particles are carried out of the settling chamber and are caught in paper thimbles fastened to the discharge of the settling chamber. After a sufficient time has elapsed to permit all 0 to 5-micron particles to pass up through the settling chamber and into the paper thimbles, the air supply is cut off and the weight of powder caught in the thimble is determined. All particles larger than 5 microns in size settle back into the U-tube and another clean paper thimble is attached to the outlet of the settling chamber. The air flow is then increased to an amount just sufficient to carry all particles in the next particle-size range up through the settling chamber and into the paper thimble. Settling chambers of several sizes are conveniently arranged to be interchangeably attached to the U-tube, thus permitting the coarser micron ranges to be successively separated without increasing unduly the volume of air required. The velocity of the air entering the U-tube is held within certain fixed limits, high enough to ensure proper agitation, but is held low enough to prevent actual grinding of the powder sample. This is accomplished through using a tip of the proper size on the air jet, several tips of different diameters being supplied.

The particle-size distribution is determined by weighing the various fractions thus separated. While this method takes more time for an analysis than the Wagner, it has the advantage over the other methods considered of retaining each separate cut so that the various fractions separated can be examined microscopically for calibration purposes, and these samples can be used for various experimental purposes. The fractions made by the Roller analysis are not 100 per cent sharply divided into the definite micron ranges but appear to show a definite overlapping of particle sizes in the different ranges. However, this overlapping does not appear to be serious and very satisfactory results have been obtained on metal powders with this equipment, these results checking fairly well with both microscopical and Wagner determinations. In calibrating the Roller instrument, and also the Wagner, it is probably advisable to check results against some other method such as the microscopical count.

Inasmuch as paint applications demand testing methods distinctly different from those for powders entering the field of "powder metallurgy," and since such methods are not believed to be primarily metallurgical problems, tests for paint have not been included in this paper. Such methods are fully covered elsewhere.[17]

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DISCUSSION

[For discussion, see page 70.]

Types of Metal Powder Products—a Classification

By Gregory J. Comstock*

(New York Meeting, February, 1938)

There is a growing interest in the possibilities presented by the manipulation of metal powders, which justifies an attempt to summarize their character and potential value. A summary of this kind presents an opportunity for making a classification of metal powder products into several general types.

Our present knowledge of the finer and more abstract aspects of many of the principles involved in metal powder technique is extremely limited. Any conclusions as to the ultimate value of the process will, therefore, for the present at least, be of doubtful value unless they are substantiated by its products. The number of such products is increasing. A study of their diverse and unusual characteristics; an examination of the methods by which they are made, and a consideration of the reactions that take place during their fabrication, in so far as we can define them, should afford as good an evaluation of this interesting development as it is possible to make at this time.

A critical study of this kind results in a formidable list of special attributes, which apparently are characteristic of applied powder metallurgy. A comparison of these special effects with the end products and well defined limitations of the melting and casting process indicate that often they may very well be considered as being special advantages. They are subject, of course, to certain not as yet so well defined limitations of their own. Based on current products only, a necessarily condensed summary of the more striking special attributes of the metal powder process follows.

MANIPULATION OF HIGHLY REFRACTORY METALS

The powder process presents a means of manipulating highly refractory metals, which cannot be cast and formed in the usual melting and casting process. Tungsten, molybdenum and tantalum are the classic examples of the adequacy of the metal powder process for meeting unusual conditions of this character. The development and application of these metals by means of it, and their importance in the electrical

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Manuscript received at the office of the Institute Feb. 17, 1938.

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field, is too well known to require discussion here. It is interesting to note, however, that in spite of the uncertainty which still apparently exists with regard to the nature of the bond, which has been developed between the original fine particles of tungsten by sintering technique, there is no doubt whatever of the tremendous ultimate strength of the metal that has resulted from this original structure. From this example, therefore, it might be safe to assume that under optimum conditions certain of the metals in powder form may be resolved to a continuity without melting, which is responsible for producing grain or particle adhesion that is not inferior to the intercrystalline bonding of the products of casting.

FORMATION OF AGGREGATES

Metal powder technique permits the formation of aggregates in which the physical characteristics of the individual metallic components are maintained practically unchanged. Hard cemented carbide materials may be used as an example of this unusual attribute of powder metallurgy. The extreme hardness of the metallic carbides of tungsten, tantalum and titanium are maintained proportionately with their presence in these effective powder products, which otherwise would lose their most significant property. Taking advantage of this possibility of powder manipulation, it has been possible to develop a nice balance between the hardness of the carbide and the toughness of their binder alloys, and by this means to produce a series of hard metal powder compositions, which adequately meet a widely varied field of application. Similarly, the electrical conductivity of copper and the refractory strength that is demonstrated by tungsten at elevated temperatures, have been maintained proportionately and balanced in a series of metal powder compositions which are especially suitable for welding electrodes and similar applications. Powder products combining silver with graphite or silver with nickel, tungsten or molybdenum are also being made in quantity and are quite generally applied as contacts for electric interrupting devices. Their fabrication from powders proportionately maintains the desirable characteristics of their components. The fact that the latter compositions combine metallic elements that have no great miscibility with one another increases the interest in the possibilities presented by this difference between metal powder technique and the more normally applied methods of producing combinations of the metals. The property of maintaining the identity of powder components is, however, not necessarily confined to metals or nonmetals that do not alloy with one another. Tungsten carbide is soluble to a limited extent in its most common binder, which is metallic cobalt. Powder manipulation of these components can be regulated so that controlled alloying during sintering is effected, with the result that the identity of the carbide is either practically unaffected or is modified by the alloying that is permitted to take place.

The opportunity for combining metals and perhaps nonmetals and alloys in powder form without materially changing their individual characteristics presents an interestingly different and perhaps fundamentally significant metallurgical possibility.

FORMATION OF UNUSUAL STRUCTURAL EFFECTS

The use of metal powders promotes the formation of unusual structural effects which do not result from other methods. For certain purposes, compacted metal powders may be heat-treated under conditions that do not promote the formation of any liquid constituent—as happens with some of the copper or silver refractory compositions just mentioned. Particle to particle adhesion is promoted by contact welding, consequently none of the typical cast structures or the products of selective solidification from a melt are developed. Grain or particle size is primarily regulated in the finished products by the initial grain size of the powders employed, as is also the distribution of the metallic constituents. In other words, the structure of these materials is predetermined and their components are distributed by prearrangement without the necessity for considering any intermediate structure, which must be altered to conform with the final structural arrangement desired.

There are at present several applications of metal powder practice by which local variations in composition are effected throughout the mass of the product in a manner that it would be difficult to conceive of being produced by other means. One of the more complicated examples of this kind consists of a powder metal disk, sections of which are permanent magnets set in the nonmagnetic sections of the unit. This composite is quite simply produced by introducing the powder components of the magnetic sections into a sectional form, which is temporarily placed in the compacting die; similarly, introducing the nonmagnetic component, withdrawing the form, and pressing, sintering and magnetizing the disk that results from these operations. Bimetallic electric contacts have for some time been produced by placing powdered copper in a mold, adding a layer of powdered silver and graphite or other suitable powder mixture, and pressing and sintering the composite to the contact form. These and many similar examples might be mentioned, all of which are illustrative of the interesting possibilities for structural variations in composition that are rendered possible by powder manipulation.

The regulated porosity of the copper-tin-graphite bearing, which is now being manufactured in quantity from powders, is another extremely important example of the unique possibilities presented by this phase of metal powder manipulation. Pore continuity and void capacities, as well as the strength and heat conductivity of the bearings, are controlled with increasing accuracy as a more complete knowledge of the principles involved in their manufacture from powders is accumulated and applied.

Based on an evaluation of the present products only, it is evident that the structural effects that can be promoted by metal powder processes presents possibilities which are of considerable proportion.

ALLOYING BY DISPERSION OR LOCALIZED FUSION

The manipulation of metal powders permits alloying by dispersion or localized fusion between adjacent particles and the production of alloy parts or articles that are practically in their final form. This is one of the latest to be developed and at present least applied of the possibilities of powder metallurgy. The porous powder bearing is, in one sense, an example of this type of powder alloying, inasmuch as certain of the primary powders of which it is originally composed combine during heat-treating operations. The porosity of these bearings may be said to be the principal consideration of their fabrication, however, and the development of alloying by diffusion between adjacent particles incidental to it. It has been repeatedly demonstrated that hot-pressing powder mixtures of copper and zinc results in brasses that essentially respond to subsequent mechanical or thermal treatment in a normal manner. The iron-nickel-cobalt magnet, as well as a recently developed magnetic alloy that presents extremely severe casting and finishing difficulties, is tentatively being produced from powdered constituents. While there is not a great deal of information available with regard to this latter development, it is assumed that the elimination of cast structures, the desire for maintaining a fine grain size, ease in processing to final conformation, and the possibility of forming a satisfactory material by fusion and dispersion alloying effects between adjacent particles of the powdered constituents of these magnets, were factors that influenced the selection of the powder process as a means of manufacturing them.

There is some evidence, therefore, which can be based upon materials that are currently being made, that the production of powder alloys presents definite possibilities for making articles that involve forming difficulties. It is true that at present this faculty of metal powder technique is either employed to produce the usual cast compositions more economically than can be accomplished by normal means or is incidental to some of the other functions of the powder process. That satisfactory local alloying from powders can be accomplished at the same time that shaping or forming operations of a final character are being applied seems to present a possibility of an extremely interesting and important nature. Its application to alloys that are difficult or impossible to form, or which involve impractical casting technique is anticipated.

Powder Methods Avoid Melting and Casting Difficulties

Metal powder methods are not subject to some of the limitations of melting and casting. Possibly the production of metallic tantalum in the form of sheet, strip or rod illustrates better than any other single example this capacity of the metal powder process for meeting certain inadequacies of other methods. It is most certainly a notable accomplishment by any means. This curious metal is highly refractory, its melting point being over 2800° C. It has a tremendous affinity for certain gases and when heated in hydrogen, for example, will absorb over 700 times its own volume of that element. When hot it forms a carbide readily. It loses its characteristic and valuable ductility in consequence of this fact if it is brought into contact with carbon or carbon-bearing gases at elevated temperatures. It oxidizes with increasing rapidity as temperatures are raised above 400° C. and will ignite and burn freely in oxygen at temperatures higher than 600° C. If melting and casting were the only available means of producing metallic tantalum, these characteristics of the metal would, therefore, impose the necessity of generating casting temperatures higher than 2800° C., in carbon-free and gas-free atmospheres and of conducting both the melting and casting operations from this high temperature with oxygen rigidly excluded from contact with the metal. Fortunately, powder methods are not subjected to some of the difficulties that would be incident to operating under these circumstances. Powder compacts can be heated and cooled in vacuum without the manipulation difficulties unavoidably incident to vacuum heating and casting. The form of such compacts are maintained without further molding during the heat-treating, fusing or sintering operations applied to promote adhesion and the development of strength and ductility in the metal forms that are resolved by these means from the compacted powders. The exclusion of carbon-bearing or other gases is quite feasible in these operations of the powder process. As the temperatures involved in the process are lower than the melting point of the metals being fabricated, electric resistance or induction heating can be employed, which does not involve either the products of combustion or oxidation. Protective slags or additions to promote fluidity of casting are not necessary, nor are deoxidizing or degasifying additives, which so commonly result in compromise effects of an undesirable character. Extremely high purity is possible, therefore, when primary metallic elements such as tantalum, tungsten or molybdenum are produced by these means. High purity and exact composition regulation are possible when metallic powders are combined in this technique, as is so well illustrated by the high accuracy of the hard carbide compositions now being made.

The possibilities of the metal powder process which may be illustrated in this manner would be well worth considering if they only afforded an easier commercial application of vacuum heating than is at present generally available. When, in addition, they give evidence of supplying means for manufacturing products of unusual purity, and of removing the necessity for employing additives that are undesirable in the final products themselves, their general trial application to a wide variety of materials seems to be unmistakably indicated.

Molding Metal Powders Economically

In some cases, metal powder production is more economical than other methods. Illustrations of the fact that it is possible to save money by molding metal powders directly into the form of certain finished articles are becoming more numerous. Commutator segments, other small motor parts, magnets and iron bearings may be used as examples. Experiments indicate that the production of coins by this method would possess some advantages over the process that is currently being used for manufacturing them. Round objects blanked from flat sheets or strip unavoidably result in a high proportion of scrap, which must be remelted and again reprocessed into sheet from which the same proportion of scrap is again produced. Coinage alloys that include a precious metal require an extremely exact composition control, which adds materially to the cost of melting. Also, when the weight of the coin depends solely upon the thickness of the sheet from which it is blanked, increased costs are involved in maintaining the necessarily exact gauges of the sheet from which the coin blanks are punched. Tableting machines originally made for the exacting requirements of pharmaceutical application have been developed to produce powder metal preforms of surprisingly uniform weight at high speed. Alloyable mixed metal powders preformed in this manner and sintered in furnaces having controlled atmospheres could be coined to high density without involving the production of any scrap by the necessary removal of excess material. It seems surprising that this process is not being more definitely developed for the manufacture of coins, particularly where precious metals are involved. The production of bearings sufficiently accurate in size to meet the exacting tolerances necessarily imposed upon them has involved high production costs. Forming them from powders has apparently decreased these costs, promoted uniformity and at the same time permitted composition and structural changes that have increased the efficiency of these essential parts. The economic possibilities of forming metal powders directly into finished products are becoming more generally demonstrable. It is possible that some part of the increasing general interest in the manipulation of powdered metals is attributable to this fact. Further information must certainly be obtained on many of the adhesion effects involved in such molding operations, and possibly more familiarity in handling powders must be developed before it will be possible to estimate accurately the savings that can be expected by any very general application of the process to the production of finished articles.

COMMERCIAL PRODUCTS

The principal commercial products now being manufactured in quantities from metal powders are four in number: (1) the refractory metals, (2) hard cemented carbides, (3) bearings and (4) contact materials, which have been used for purposes of illustration. The refractory metals are processed in powder form because no other means is available for adequately working them and because this art has been devised to meet their requirements. Hard carbide compositions, also, can be made only by powder methods without sacrificing the valuable physical characteristics of their major constituent. No structural effects similar to those displayed by the porous bearings have been developed by any other process than those involving the use of powders; consequently they are made from them. The special materials used so effectively as welding electrodes and other electric contacting surfaces are made from powders to maintain the identity of the components and to effect combinations of metals that otherwise would be impossible. All of these products may be said, therefore, to owe their development to the possibilities presented by powder metallurgy and to be made from powders from necessity rather than from choice. Their practical manufacture on a large commercial basis has established the efficacy of the powder process for producing unusual materials and meeting conditions when other better known methods are found wanting. The powder process has produced the strongest of the metals—tungsten; the hardest of the alloys—hard cemented carbides; structural effects of an important nature, which cannot be otherwise produced—the porous bearing; and the mechanical union of unalloyable metals—electrode and contact materials. The combined industrial effects of these products has been very great. Closer scrutiny of the process and the products made by it in smaller amounts than the four types of materials that have been mentioned—or are in process of being developed by means of it—shows that it gives promise of affording possibilities of a high order of desirability when it is applied to materials that can be made by other means. The process demonstrably affords a means of obtaining extremely high purity; of easily applying vacuum or controlled gas atmospheres; development of further desirable structural or localized composition effects; elimination of cast structures and the undesirable addition of materials to promote casting; the possibility of forming difficultly forgeable or castable materials and, in some instances, the production of articles cheaper than they can be made by other methods. Even a very condensed summary of the potentialities of powder metallurgy based on the current products that are made by means of it indicates its importance and eminently justifies the serious consideration at present being given to its future development.

The present products, therefore, fall into a natural classification of two general types: (1) products that cannot be made by other means; (2) products that can be made more efficiently or more cheaply from powders than by other processes. The four principal commercial products just mentioned are in the first class; the more recent and less generally known powder products that have been used as an illustration of the individual possibilities of this new art are chiefly in the second class (Table 1, A grouping).

It should be noted that in classifying current powder products into types, commercial products have been mentioned for purposes of illustration and that no effort has been directed toward making a complete list of the products that are now being manufactured. The commercial development of these materials is naturally surrounded with a certain amount of reserve when the finer details of fabrication and composition are concerned. A complete list of the powder products that are being made or are in process of development would, therefore, be difficult, if not impossible, to make at the present time.

Another grouping of powder products could be made on the basis of one important phase of their fabrication (Table 1, grouping B). Those in which it is desirable to form a liquid constituent during their heat-treatment could quite properly be differentiated from those in which particle adhesion is promoted without fusion.

All four of the principal commercial products now being made from metal powders originally emanated from the electrical industry, because metal powder processes were first developed on a large scale to meet the production requirements of the filament of the electric lamp. Those engaged in the research, development and production involved in the manufacture of filament materials were responsible for the development of the powder technique and the special equipment required by those products. Their first-hand experience and familiarity with the metal powder manipulations they had developed, and the special equipment that was at their disposal, naturally resulted in their being the first to apply the possibilities of the powder process to the development of such new products as were of interest to them. These original commercial powder developments extended over a period of many years. They involved the expenditure of large amounts of pioneering effort and capital. They have, therefore, quite properly been surrounded by a more or less transient patent structure, which is calculated to assure a return upon these investments. This localizing of information and experience to one industry, and more recently to associated industries, has had its good and its bad effects on the general application of powder metallurgy. All of the resources of a large engineering industry have been brought to bear upon the difficulties involved in the first practical application of the powder process. It appears most unlikely that the current metal powder products could have been advanced to their present commanding position in industry without such help. On the other hand, now that the potentialities of this new art have been so ably demonstrated, its application to other and possibly broader industrial fields is, to a certain extent, hampered by a lack of general knowledge and experience, which may in part be attributable to the manner in which it was originally developed. These difficulties, fortunately, are of a temporary

TABLE 1.—*Types of Current Metal Powder Products*

A GROUPING

Materials That Can Be Fabricated or Worked Only as Powders	Materials That Can Be Made by Other Means but Can Be More Efficiently Produced from Powders
Highly refractory metals—tungsten, molybdenum, tantalum	Materials forged or cast with difficulty, such as permanent magnets
Hard cemented tool materials	High-purity material from which it is desirable to exclude additives to promote casting
Porous bearing materials	Iron-nickel-cobalt alloy, titanium-copper
Electrode and contact materials	Articles that require excessive machining or involve considerable scrap in their production—small parts, coins, etc.
	Composite parts or articles that can be made from powders more easily by localizing composition effects—valve parts, etc.
	Parts or articles adversely affected by cast structures, such as magnetic alloys, thermostatic alloys

B GROUPING

Powder Products Fabricated without Obvious Formation of Any Considerable Quantity of Liquid Constituent during Heat-treatment	Powder Products of Which the Fabrication Involves Cementing by Formation of Considerable Quantities of Molten Constituent during Heat-treatment
Refractory metals	Hard cemented carbide compositions
Certain contact alloys, such as those high in silver or copper and low in nonmetallic or refractory metal content	Contact and electrode materials made by impregnating porous compacts with molten metal
Pure metal powder products such as copper commutator segments, low-carbon iron bearings, etc.	Porous bearings that involve melting a component of impregnation with molten metal
	Products involving fusion alloying, such as the magnetic powder alloys
	Certain powder-faced materials such as those in which fusion surfacing with hard carbides is employed

nature. They indicate unmistakably, however, the necessity for further investigation and study of the fundamentals involved in manipulation of metal powders, and the dissemination of this information when it has been obtained for general application to any field in which it may be required. In view of these circumstances, it would seem that a study of the finer points of powder metallurgy would present an unusually fertile field of research for college or university investigation.

The products of powder metallurgy unmistakably indicate the unusual possibilities presented for further development. The unique character and performance of these products have awakened a genuine interest in ascertaining the effects that can be produced by other applications of metal powder practice. It is believed quite generally that the effects of such future applications will be of far-reaching character. At present, they are temporarily delayed by patent barriers, lack of fundamental knowledge on many essential points and by a scarcity of first-hand experience and familiarity with the manipulation and equipment that has been developed for the present practice of applied powder metallurgy.

Acknowledgment

Acknowledgment is made to Mr. Robert H. Leach, Vice President of Handy & Harman, for his kind cooperation, and to that company for facilitating the preparation of this summary of metal powder products.

DISCUSSION

[For discussion, see page 70.]

Ductile Tantalum and Columbium

By Clarence W. Balke

(New York Meeting, February, 1938)

Small buttons of fused tantalum have been produced by arc fusion in a vacuum, by drawing an arc between sticks of pressed tantalum and a tantalum-faced water-cooled copper block. However, ingots of appreciable size can be produced only by the heat-treatment of bars pressed from powder. The following outline covering the production of finished bars of tantalum by the methods of powder metallurgy is also used for the production of columbium, taking into account the difference in the melting points of these two metals.

Pressing the Powder

With possibly a few exceptions, a pressing operation is one of the essential steps in the practice of powder metallurgy. In fact, the author's experience with a number of high-melting-point metals and with numerous types of hard carbide compositions has led him to believe that this operation is often one of the most important in the entire process, and frequently one of the most difficult to carry out in a satisfactory manner. Defects due to improper pressing can readily lead to a defective finished product. It is the author's opinion that rarely is a bar or other article pressed from metal powder in such a way that all parts of the piece are uniformly pressed. The nearest approach to uniformity of pressing is possibly attained when the powder is contained in a flexible receptacle, such as rubber, and is pressed under a liquid by hydrostatic pressure. However, this method is not generally applicable. Hydraulic pressing in steel dies where one or two punches are forced into the die must usually be resorted to. As the pressure in such a die is built up, the powder begins to cling to the walls of the die with a tenacity dependent upon the nature of the powder, and this results in a bridging action, so that the layers of powder adjacent to the moving punch are pressed more heavily than those further removed in the mass. Frequently, as the pressure is carried higher, there may be a mass slippage of the powder upon itself, with the result that slip cracks are formed within the pressed

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Manuscript received at the office of the Institute Feb. 1; revised April 8, 1938.

* Director of Research, Division I, Fansteel Metallurgical Corporation, North Chicago, Ill.

piece. These slip cracks may not be healed by increase of pressure and frequently cannot be healed or repaired in the sintering operation.

Tantalum powder can be pressed more easily than powders of much finer particle size. The high ductility is also an aid in pressing. But even with this, using a single-punch die, one side of the bar is always pressed harder than the other. The shape of tantalum bars is varied, depending upon the use to which they are to be put. Bars intended for rod or wire are pressed square and weigh about 2 kg. Bars intended for rolling are pressed into a rectangular shape, weighing from 2 to 3 kg. The pressure used is of the order of 50 tons per square inch. With electrolytic tantalum powder not too heavily gassed with hydrogen, this operation produces an appreciable amount of cold welding or cold sintering and the bar is strong enough to be clamped under considerable pressure in water-cooled terminals within the vacuum heat-treating furnace. The grains of tantalum metal undoubtedly are coated with a film of oxide. During the pressing operation, however, this film is ruptured at points of contact, with the result that sintering forces can come into play and produce an appreciable amount of bonding.

Heat-treating Tantalum Bars

The amount of current required to produce a definite temperature on the surface of a pressed tantalum bar when heated by its own resistance within an evacuated chamber must of necessity be varied in relation to the particle size of the original powder and to a smaller measure upon the pressure applied in producing the bar. As the coarseness of the powder increases, the heat gradient from the center to the surface of the bar will increase. This factor establishes a definite limitation upon the maximum cross section of a bar that can be satisfactorily heat-treated in this way. As the cross section is increased, a point is reached where the surface temperature of the bar is not sufficiently high to produce satisfactory results at a time when the temperature at the core has reached the melting point. The use of baffles around the bar to reduce this heat gradient has not been found very practicable. Because of these variations—that is, electrical conductivity and variations in heat gradient—it has been found necessary to vary the heat-treating schedules according to the classification of the grain size of a given lot of powder.

Each individual lot of tantalum powder is made as large as possible and classified as to its relative grain size against standards for which sintering characteristics have been determined by extensive experimentation. A pilot bar from this lot of powder is carried through all the steps and finished sheet is produced before this lot of powder is released for production. The bar is clamped in a vacuum sintering furnace, which is then evacuated to a residual pressure of only a few microns. An electric current is passed through the bar and the temperature is gradually raised until the core is very close to the melting point of the metal. The amount of current necessary is measured on an ammeter, which has been calibrated against previous bars in conjunction with the use of an optical pyrometer, reading the surface temperature of the bar through a quartz window in the wall of the furnace. Constant calibration and check of these measuring instruments is necessary and the actual current employed is selected from calibrations that have been made against pressed tantalum bars of varying grain size. For tantalum, this heat-treating operation must accomplish what is usually accomplished with tungsten or molybdenum and, in addition, must eliminate the absorbed gases originally present in the powder. For this reason, the heat-treatment must be extended over a longer period of time than is customary with tungsten or molybdenum and must be continued until the vacuum gauge attached to the furnace indicates that the removal of these gases has become complete.

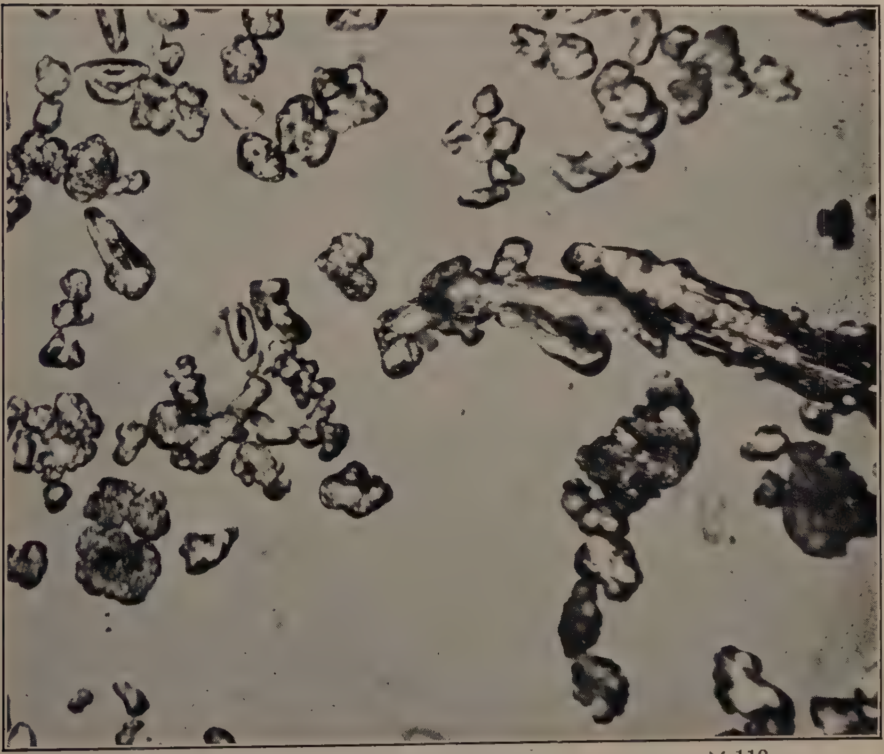

FIG. 1.—TANTALUM POWDER OF NORMAL PARTICLE SIZE. × 110.

Great improvements have been made in the heat-treating furnaces and pumping equipment, so that the time required for this operation is not excessively long. When a tungsten or molybdenum bar is heat-treated, there is an appreciable amount of shrinkage. While no corresponding amount of shrinkage takes place in a bar of electrolytic tantalum, a small amount of shrinkage does take place, but the bar is still porous and a heavy mechanical working becomes a substitute for the shrinkage that occurs in metals made from finer powders. The completion of the sintering operation is then accomplished by a second heat-treatment in vacuum. In this second heat-treatment differences existing in the first treatment due to variations in particle size have been eliminated and a uniform schedule can now be adopted for the sintering operation.

A portion of this pilot bar is rolled to sheet and given a thorough vacuum anneal. The sheet is examined for possible surface defects that would be present if all porosity had not been eliminated, and the percentage of elongation when pulled in a testing machine is measured. If this sample sheet passes this inspection, the entire original lot of powder is released for production and is handled by the schedules that have been found satisfactory for the pilot bar. Metallic tantalum produced in this way is ductile at room temperature and can be rolled, drawn, spun and swaged, all at room temperature.

The great affinity of tantalum and columbium for all common gases has led to an extensive use of the metals in the vacuum-tube industry. The remarkable corrosion resistance of tantalum has resulted in its use for the construction of equipment used to handle corrosive materials. The great hardness of the carbides of tantalum and columbium, and the peculiar properties imparted by them, account for their use as constituents in hard carbide compositions. For a more detailed account of the applications of tantalum, see *Industrial and Engineering Chemistry* (1935) **27,** 1166 and (1938) **30,** 251.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance rendered by Mr. Claire C. Balke, who has done very valuable work in connection with the metallurgy, metallography and sintering of tantalum and columbium.

DISCUSSION

(*T. S. Fuller presiding*)

[This discussion applies also to the papers beginning on pages 37 and 57.]

M. L. GRIFFIN,* Taunton, Mass.—This is entirely new matter, and fundamental. I have visualized all materials as passing through three states of aggregation. As I looked upon one of the samples a few minutes ago, I was asked, "What state do you credit these?" I said, "Approaching liquidity." It is very evident that the mechanical process of making these powders is on the way. It is on the way visibly in this exhibit to the molecular state of aggregation, and when the processes are carried on farther by the addition of heat and pressure, the atomic state and complete liquidity will be approached. And you will find, I am sure, that as you continue the progress of this matter, you are acquiring atomic power.

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* Consulting Chemist.

G. W. Jarman, Jr.,* New York, N. Y.—Mr. Comstock mentioned four uses for metallic powder. There is another use, which has had extensive development abroad but is limited to the low-melting-point materials—that is, under 1000° C. In England, particularly, there is in use a process for the coating of steel or iron surfaces against corrosion that uses a combination of silica and zinc powder to coat the surfaces. The powder is applied through an oxyacetylene flame onto a prepared or sandblasted surface. This method has been adopted by the British Admiralty for submarine construction against sea-water corrosion. The powder can be used either in a relatively coarse size, such as minus 150, or in some instances, such as zinc dust, with a large portion of it minus 325 mesh. It is applied rather rapidly at about the cost of a good application of paint after the preparation of the surface. It is also applied to concrete tanks. Many European nations are building storage tanks for oil and other materials underground. I understand that France has made plans for building underground tanks for all kinds of liquids as well as for storage of war material. (Mr. Jarman exhibited a concrete slab that had been coated with tin and then buffed.)

F. E. Carter,† Newark, N. J.—The sintering is done at about two-thirds of the melting point. Does that limit the temperature at which the alloys made by powder metallurgy can be used later? Can you use it later on above 1100°?

E. Fetz,‡ Newark, N. J.—The speakers of this morning's symposium on powder metallurgy have given an excellent bird's-eye view of the industrial advance of this new branch of metallurgy and a résumé of the commercial aspects of powder metallurgy. We have all marveled at the remarkable accomplishments of the industry, which, under the leadership of men like Mr. Hardy and the other speakers, is blazing the trail.

Lately, science seems to take an interest in this new field, and science certainly will be amply rewarded. Attention may be called to some of the many unsolved problems and to some of the features wherein powdered metals differ from polycrystalline solidified metals. Scientific investigations should be attracted in particular by two unique features—purity and porosity—as many of the physical, chemical and mechanical properties are intimately related to these two.

There is no denying that the establishment of all physical properties of the metals in the pure state is of paramount scientific interest. We know the phenomenal effect of certain impurities upon some physical properties such as hardness, tensile strength, electrical conductivity, temperature coefficient, corrosion resistance, creep, fatigue, recovery from cold-working, recrystallization, etc. Since contaminations cannot be often avoided in the orthodox processes of smelting and refining, powder metallurgy offers an indispensable tool for research along this line.

The preparation of metal powders by reduction of their oxides, chlorides, hydrides, by precipitation from gas compounds such as iodides, carbonyls, followed by compression, sintering, plastic deformations and intermediate recrystallizations, has furnished some high-purity metals suitable for determination of their true physical properties. Contrary to previous findings on these metals prepared by the conventional methods, the powder metals proved to be partly very ductile so that hot-working or hot and cold working became possible. For instance, while electrolytic and thermite chromium has a hardness of several hundred Brinell units, chromium made from powder by reduction of its oxide through calcium may have a hardness as low as 120 Brinell.

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* Separations Engineering Corporation.

† Physical Metallurgist, Baker & Co., Inc.

‡ Research Metallurgist, Wilbur B. Driver Co.

Particularly sensitive to impurities seems to be the recovery of certain physical properties from cold-working as shown by hardness, tensile and microscopic tests on nickel made from carbonyl powder. While commercially pure nickel loses its work hardness between 600° and 700° C., carbonyl nickel of high purity softens between 300° and 400° C. The drastic effect of impurities has been proved by small additions of powdered elements to the carbonyl nickel powder. The powder method was applied to avoid contamination by crucible and deoxidizer.

No hypothesis has been advanced yet why some impurities are so effective. A qualitative and quantitative study of the effect of elements added individually and combinedly on the physical properties of high-purity metals offers a wide field for scientific work along powder metallurgical lines.

It should not be overlooked that powders prepared by entirely new methods usually contain impurities, too, but of a different nature from those in ordinary metals. As many of these impurities cannot be determined by spectroscopic means, improvement of our present analytical methods offers to science a further field of activity connected with powder metallurgy.

A second group of phenomena observed on powdered metals is connected with the grain boundary, which in sintered metallic bodies appears to be markedly different from that of cast metals. No matter how excellent hardness and tensile strength of sintered-metal compacts, their ductility is comparatively low. There is no simple relationship between strength and hardness contrary to ordinary metals. At low sintering temperatures, a low tensile strength is often found in conjunction with high hardness values. Although soft powdered metals such as chromium and beryllium have been prepared, they still refuse to be cold-worked, probably because of their peculiar boundary conditions.

The storage of energy induced by cold-working must be considerably greater in metals prepared by sintering compressed powders than in ordinary metals, as revealed by carbonyl nickel powder samples that have been inadequately plastically deformed. They lose their work hardness in a phenomenally low temperature range. On long-time annealing, softening takes place below 200° C. By increasing the number of plastic deformations and recrystallizations, the recovery temperatures are progressively shifted to higher temperatures.

The scientifically and practically important hypothesis that the fine grain and consequent larger energy absorption are responsible for the greater vibration amplitude of the atoms and lower hardness recovery temperature has been confirmed on less pure electrolytic nickel, which, in the as-deposited state, may have a very fine grain size. According to unpublished experiments, the recovery range of the electrolytically deposited metal can be progressively shifted to higher temperatures by annealing at rising temperatures prior to plastic deformation.

The absorption of a greater amount of latent energy shows up in the mobility of the atoms in the space lattice and recrystallization in the various nickel powder samples also took place at abnormally low temperatures. The greater storage of latent energy may be partly responsible for the limited plastic deformation ability of powdered metals as compared with ordinary metals. This appears to be further aggravated—particularly with very small grain—in so far as the applied external forces cease to operate at a very small distance into the body of the mass. The stress distribution in powder metals seems to be a problem worth scientific investigation.

It has always been a matter of conjecture as to what is responsible for holding together compressed powder, and it appears possible that the cohesional forces or the ability of the surface atoms to affect each other far below the melting point are greatly influenced by the pressure and occurring induction of latent energy. This effect may manifest itself in hardness tests. Trzebiatowsky, for instance, obtained about 200 Brinell on cold-pressed and still porous copper powder while ordinary metal shows a maximum strain-hardening of about 120 Brinell. This phenomenon certainly challenges scientific interpretation. It can hardly be explained on the basis of work-hardening of individual grains.

Grain growth in powdered metals may be quite different from that in ordinary wrought metals because of the impeding effect of the grain-boundary substance or because of porosity. This effect was brought out by a recent study of recrystallizing melted carbonyl nickel and sintered nickel powder, and has been practically utilized for a long time by artificial additions of thoria to tungsten powder in order to check grain growth in filament wire. Early attention was also focused on the grain boundary of tungsten because it exhibited *inter*crystalline fracture while most metals break *intra*crystalline.

Further problems worth scientific investigation are related to diffusion speed along grain boundaries as compared with lattice diffusion, adsorption of gases and vapors in powdered metals, diffusion rates of gases and their solubilities. Naturally, the greatest amount of interest is focused on the sintering process, which plays a predominant role in powder metallurgy. While cohesional forces decrease with temperature in ordinary metals, compressed metal powders become stronger on exposure to rising temperatures. It might sound paradoxical, but this is partly because of an increase of plasticity and partly because of the improvement of the contact between the powder interfaces.

Unfortunately, physical tests on powdered metals at elevated temperatures are few, although the most astounding effects may be expected. By hot-pressing of very fine copper powder at 500° C., Trzebiatowsky obtained a hardness of 120 Brinell. In the first place, such a hardness can hardly be duplicated with cast copper and in the second place, the recrystallization temperature of ordinary, severely cold-worked copper is close to 100° C.

As may be inferred from these few examples, unique properties may be obtained with powdered metals which cannot be reproduced by cast metals. The observed phenomena certainly challenge scientific interpretation and further studies along powder metallurgical lines are bound to shed new light on the science of metals.

T. S. Fuller,* Schenectady, N. Y.—The papers this morning have impressed me again with the fact that one of the most important fundamental properties with which we have to deal is diffusion. This property must be considered when attempting to account for the brittle, intergranular type of fracture that occurs in metals when stress is applied for long periods of time at temperatures above that at which recrystallization takes place. The sintering of powdered metals is essentially a diffusion process, and such work on that subject as has been reported to this meeting by Dr. Mehl and others seems to me to be extremely opportune.

E. E. Thum,† Cleveland, Ohio.—One of the speakers asked about how powders are measured. At the Cleveland Wire Works of the General Electric Co., a sample is nibbed out on a biological slide and a greatly enlarged image projected on the ground glass of a camera box. The operator then counts the number of particles in several standard-sized fields, classifying each as to its size within definite dimension limits. A curve is then drawn showing the frequency of particles of each size range, and if the distribution is not such as to fall within what experience indicates will make a suitable material for processing two or more such irregular batches are mixed so as to bring the "screen analysis," redetermined as above, within the proper limits for frequency distribution.

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* Engineer of Materials, Works Laboratory, General Electric Co.

† Editor, *Metal Progress*.

I also want to mention the desirability of keeping at least one foot on the ground when considering such interesting new things as powder metallurgy, and to protest against any undue assumption that *purity* in metals increases *utility* in metals. That is merely an assumption—and, in fact, an erroneous assumption. The facts of the case do not warrant the statement. Purity of metal merely means less contamination, and does not, *ipso facto*, guarantee any superlative physical or chemical property, except perhaps a reduction of susceptibility to electrochemical corrosion. In fact, modern metallurgy aims at the control of impurities in metals rather than at the production of pure metals.

The standard illustration in regard to highest purity as a great and desirable thing is electrolytic zinc, but the principal use of electrolytic zinc is for die-casting alloys. We no sooner get it pure than we put in a lot of impurities in order to make it useful.

As to the present and future possibilities in powder metallurgy, anyone would be bold to set sharp limitations; nevertheless, as far as we can see at the present time, there is a definite limitation of size of finished part made in mass production. A powder as such will have little use except on a lady's nose, or for explosives or combustibles. If we wish to make anything coherent and more useful, we have to convert that powder into a solid mass, and that involves pressure, and as soon as we start to press any powdered material into large sizes we run across what Mr. Balke has indicated; namely, "bridging" and internal slip. Very high pressures cause serious trouble with the die materials. There are definite limitations—Mr. Bridgman brought them up yesterday*—to commercial pressures. So far as I can see, therefore, the mass production of common alloys will be for a long while limited to fairly small sizes, and commercially the process becomes similar to die casting or drop forging—small stuff and not particularly precise, and made of metal not particularly pure.

People that talk about purity and people that talk about precision in pressed and sintered material ought to be asked to define what they mean. High purity and high precision both cost so much money that the mass-production industries will not be greatly interested except for unusually fine performances. During the pressing of the powder into a die and the sintering of the compact several volume changes occur, and the product is not particularly precise as we know machine precision at the present time.

J. L. YOUNG,† Pittsburgh, Pa.—A number of the speakers have mentioned 50 tons per square inch as the necessary pressure for their work. If they were using lead powder, which is very soft, a few tons per square inch would probably press it very nicely. Many metals, if very pure, are almost as soft as lead, and for many applications a high pressure is not necessary. My work has been confined to electrolytic iron powder, which has a high purity. I have found that a pressure of 5 tons per square inch will fabricate useful articles of this material. Bakelite powders are molded at about one ton per square inch, and there appears to be little difficulty in molding articles as large as refrigerator cabinets from this material. It should not be impossible to fabricate objects of equivalent size from metal powders, provided very soft powders are used. That is the principal reason I believe in using pure metals; the metal must be very soft.

P. M. MCKENNA,‡ Latrobe, Pa.—In regard to the question asked as to the precision with which articles can be made of powdered metals: we make standard test bits that are supposed to be 0.200 in. thick, ⅜ in. wide, and ¾ in. long, and normally they come out within 0.002 in., without any particular care being taken to attain this.

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* See page 15, this volume.

† Industrial Fellow, Mellon Institute.

‡ Vice-president and Research Director, Vanadium-Alloys Steel Co.

The powdered metals can be pressed into a slug sufficiently coherent to be tested for shrinkage and then formed by cutting with a diamond or abrasive wheel to a dimension that will shrink to a very close size; say, one part in 200, or one part in 1000, which is very possible. Is not that rather precise compared to castings?

C. Hardy,* New York, N. Y.—There are commutator segments exhibited today that were pressed to measurements not exceeding 0.002 from the dimensions given by the manufacturer, the same tolerance that he gives to the manufacturer that makes commutator segments by other methods.

Dr. Balke speaks of bridging of his metals. Does that refer only to the work done by the hydraulic press? In my work I have found that as a pump works in stages, we build up air cushions and therefore layers, and the trouble is not so much with the adhesion to the side of the die as it is with air cushions that form during the compression—air cushions that expand the moment the pressure is released, and thus cause bridging and slipping of the metals. Have you tried a press that gives a blow, or a hydraulic press that will give a sharp blow or two sharp blows, and through the sharp blow force out the air and prevent the forming of air cushions? With this, there should be a slightly tapering die to allow the air to escape.

C. W. Balke.—My experience has been entirely with refractory metals, and the remark was primarily prompted by my experience with carbide compositions where this phenomenon is marked. It is difficult to press hard carbide composition without binding on the side of the die. I have never used instantaneous blows. It would seem that pressure, slowly applied, would let the air out of the powder more rapidly than a sudden blow, but I have never been able to determine that slowly loading the pressure had any different effect than rapidly loading it; that is, varying that as far as you can on a hydraulic press, hand-operated, you have quite a leeway in the rapidity of loading. I have never been able in a die of that type to completely eliminate the effect of the powder on the side of the die. What I referred to I do not believe has anything to do with trapped gas or air.

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* Charles Hardy, Inc.

Cemented Tungsten Carbide Alloys

By W. P. Sykes,* Member A.I.M.E.

(New York Meeting, February, 1938)

Seven years ago, Dr. S. L. Hoyt[1] presented a masterful discussion of the hard metal carbides and cemented tungsten carbide. His lecture summarized most of the data then available in the field; many of the details relating to the production, properties and structure of cemented tungsten carbide had never been previously published, for, in fact, this information was only then being acquired.

During the intervening years, the cemented carbides have assumed a place of real importance in the commercial field, with an ever widening variety of applications due to constant improvement in the control of production technique and the unremitting search for new compositions that might better the performance of the alloys in one or another type of service.

The most recent summary of production methods, properties and guides for the successful application of the cemented carbides appears in the 1936 edition of the Metals Handbook. Of necessity, much detailed information relating to structures and physical properties is not included in such a summary, and it is with such details that the present discussion is concerned.

Steps in Preparation

While the past 25 years have contributed a valuable store of working knowledge in the field of powder metallurgy, many of the process controls are derived entirely from experience and are not as yet finally explained by a specific physical or chemical phenomenon. For most of the cemented carbides such difficulties are aggravated by our lack of knowledge not only of the complex alloy systems involved, but also by the possible changes in structure and even in composition which may accompany variations in temperature, heating time, and furnace atmospheres.

The principal steps in the preparation of these cemented carbide alloys are fairly well known, but to supply a foundation for discussion these steps are briefly outlined as follows:

1. Formation of the metal carbide in the form of powder by heating a mixture of carbon and the metal powder or oxide for several

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Manuscript received at the office of the Institute Dec. 28, 1938.

* Incandescent Lamp Dept., General Electric Co., Euclid, Ohio.

[1] References are at the end of the paper.

hours at temperature between 1500° and 2400° C., usually in a carburizing atmosphere.

2. Intimate mixing of this carbide powder with the binding metal, usually cobalt or nickel, also in the form of powder.

3. Compressing this mixture in steel molds of various designs at a unit pressure of from 15 to 30 tons per square inch.

4. Initial sintering in some inert atmosphere, such as hydrogen, at a temperature of 800° to 900° C. to impart to the pressed metal sufficient strength for handling and shaping.

5. Final sintering at a higher temperature (in the range of 1400° to 1600° C.), which results in a considerable diffusion of the components and a real alloying action. This operation is also carried out in an inert or carburizing atmosphere.

The measurable properties such as hardness, density and strength (in the transverse rupture test) after sufficiently thorough correlation with performance in service serve effectively as controls for routine production of standard grades of cemented carbides. Metallographic inspection has proved to be extremely helpful in detecting variations in manufacturing practice and in the correction of such variations. In new compositions, however, the structures may be quite unfamiliar and their interpretation in terms of constituents or phases must obviously require extended investigation, which is time-consuming and has not as yet progressed very far. But even with an incomplete knowledge of the observed structure, certain features such as grain size and uniformity of pattern furnish a standard by which to judge the constancy of production processes.

EFFECTS OF INTERRELATED FACTORS

In a limited way, I shall attempt to illustrate by specific examples the effects of some of these interrelated factors. By increasing the cobalt content from 3 to 13 per cent in the cemented tungsten carbide alloy the density, strength and hardness change as indicated in Fig. 1. These values represent the average of hundreds of determinations made over a period of years. An individual specimen may vary from these averages by ±0.5 points in hardness, ±25,000 in strength and ±0.2 in density under well controlled conditions of production.

Structures representative of the 3 and 13 per cent Co alloys are shown in Figs. 2 and 3, respectively, at a magnification of 1500 diameters. These alloys were made from a carbide powder of medium particle size. By decreasing the particle size of the carbide powder the hardness can be raised appreciably, especially in the higher cobalt alloys, and a visible reduction of the diameter of carbide grain in the sintered product is seen in Fig. 4. The advantage of a finer grained carbide lies in a superior resistance to abrasion, which is marked in certain applications.

The particle size of the carbide powder appears to follow that of the tungsten powder, at least throughout a limited range, and is defined by the average diameter or an average volume of particle as well as the maximum in the diameter frequency curve for the aggregate of particles. The particle size of the tungsten powder is controlled by the conditions of reduction; i.e., temperature, time, depth of oxide charge and purity of the hydrogen atmosphere. Table 1 is included to show an example of the relationship between the particle size of the tungsten powder and that of the carbide produced from it.

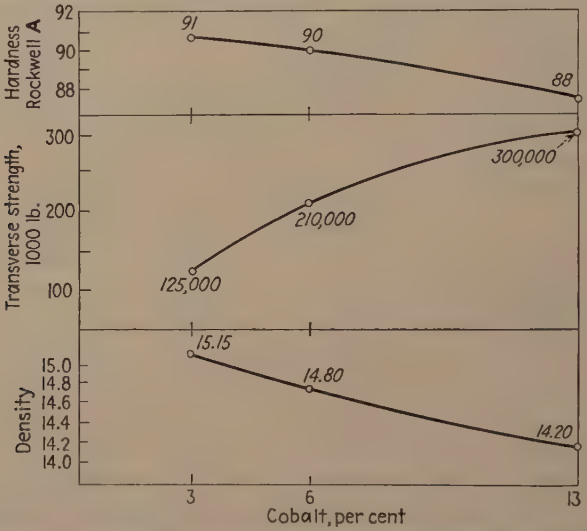

FIG. 1.—RELATION BETWEEN COMPOSITION AND PROPERTIES OF Co-WC CEMENTED CARBIDE ALLOYS.

TABLE 1.—*Example of Relative Particle Sizes in Tungsten and Tungsten Carbide Powders*

	Average Diameter, Microns	Average Volume, Cubic Microns
W, lot No. 1	2.03	18.0
WC, lot No. 1	1.34	7.5
W, lot No. 2	1.03	3.06
WC, lot No. 2	0.84	1.35

As might be expected, the sintering temperature is a factor that influences in no small measure the properties and structure of the finished alloy. In Figs. 5, 6 and 7 are shown the microstructures resulting from sintering a 6 per cent Co alloy at 1425°, 1500° and 1575° C. for 1 hr. The increase in size of carbide grain follows the rise in sintering temperature, and is especially marked at the highest temperature.

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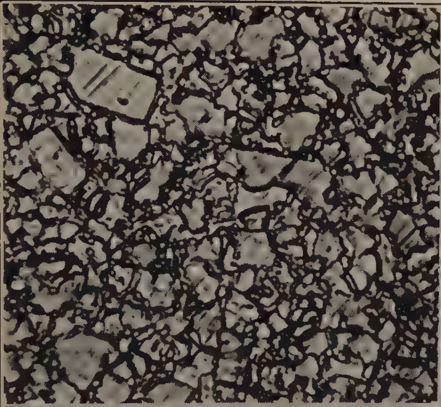

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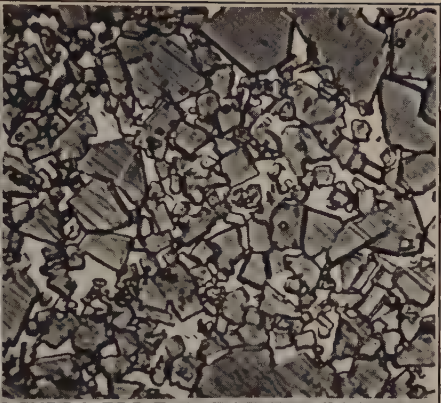

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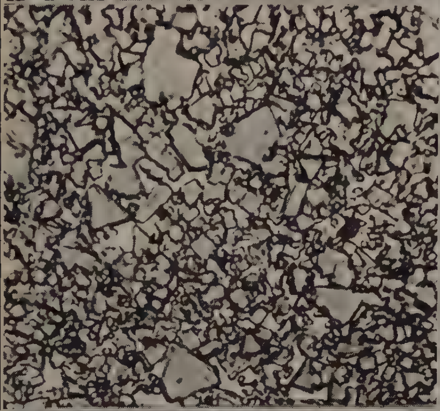

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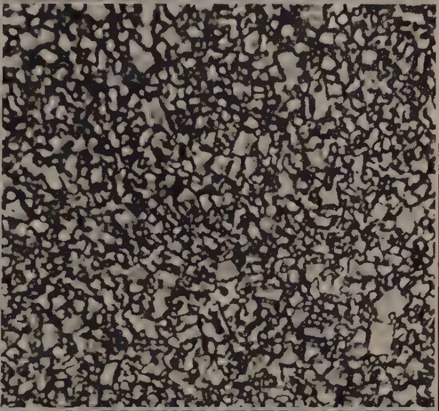

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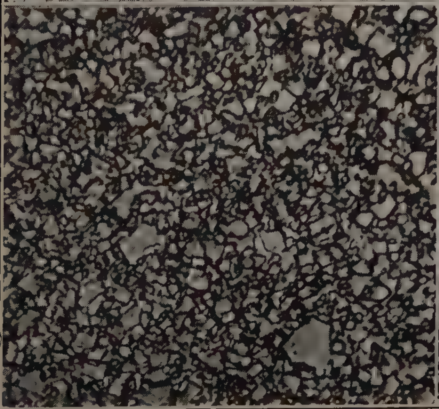

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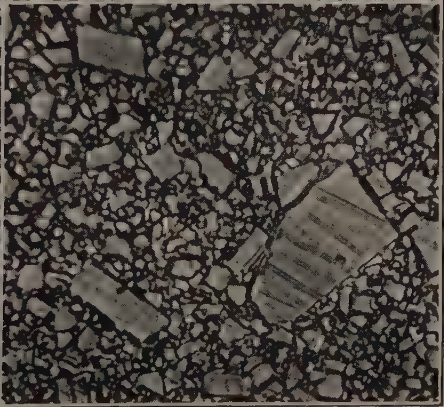

FIG. 2.—WC + 3 PER CENT. Co. Hardness, 91.3; density, 15.05; strength, 137,000 lb.

FIG. 3.—WC + 13 PER CENT Co. Hardness, 87.1; density, 14.20; strength, 318,000 lb.

FIG. 4.—WC + 13 PER CENT Co. Hardness, 88.4; density, 14.18; strength, 328,000. Made from finer carbide than alloy shown in Fig. 3.

FIG. 5.—WC + 6 PER CENT Co. Sintered 1 hr. 1425° C.

FIG. 6.—WC + 6 PER CENT Co. Sintered 1 hr. at 1500° C.

FIG. 7.—WC + 6 PER CENT Co. Sintered 1 hr. at 1575° C.

All × 1500.

The ultimate values in strength, density and uniform hardness can never be developed in the presence of many voids or physical discontinuities within the body of the alloy. Porosity is best observed in the polished section before etching and such routine observations are effective in detecting variations in current production practice. The extent and nature of the porosity are closely related to the temperature of final sintering, especially when this temperature is near the lower limit of the effective sintering range. This is illustrated by a comparison of photomicrographs of unetched sections in Figs. 8, 9, 10 and 11, which show the change in texture or soundness of the alloy brought about by increasing the sintering temperature from 1325° to 1575° C. The first increase in temperature from 1325° to 1450° C. results in a marked decrease in porosity, which is reflected in the improved values for hardness, density and strength. The changes resulting from the next increase in temperature (to 1500° C.) are slight but after sintering at 1575° C. a new type of porosity is observed in the polished section, perhaps associated with the agglomeration of the cobalt-rich cement. Positive decreases in hardness, density and strength accompany the final rise in sintering temperature.

Metallic inclusions are naturally considered as one cause of porosity. Such inclusions, however, are seldom preserved for actual observation and their action can be studied directly only when they are of appreciable size and remain in place during the preparation of the polished section. An extreme example is shown in Fig. 12, where the massive nonmetallic inclusion appearing in the center of the field is bordered by a wide fissure at some little distance on either side.

Mention has been made of the importance of furnace atmosphere in the final sintering operation. The usual temperature of 1450° C. is most easily attained and controlled in a muffle furnace heated by resistance winding of tungsten or molybdenum, which necessarily operates in a hydrogen atmosphere to protect the winding from oxidation. It is well-nigh impossible to completely exclude moisture from the hydrogen within the refractory muffle of such a furnace, consequently the alloy will be depleted in carbon to an appreciable depth below the surface if heated for any length of time in such an atmosphere. To prevent this, the work is inclosed in a carbon tube or box placed within the furnace muffle. In this way carbon is introduced into the atmosphere and ordinarily the metal is protected against loss of carbon.

An over-all carbon content appreciably lower than that demanded by the tungsten monocarbide WC is usually accompanied by excessive variations in strength between individual bars of such an alloy, although the hardness may actually increase slightly. Loss of carbon from the surface during the final sintering operation results in nonuniform volume shrinkage and impaired strength.

Because of the phasial equilibria of the systems tungsten-carbon or

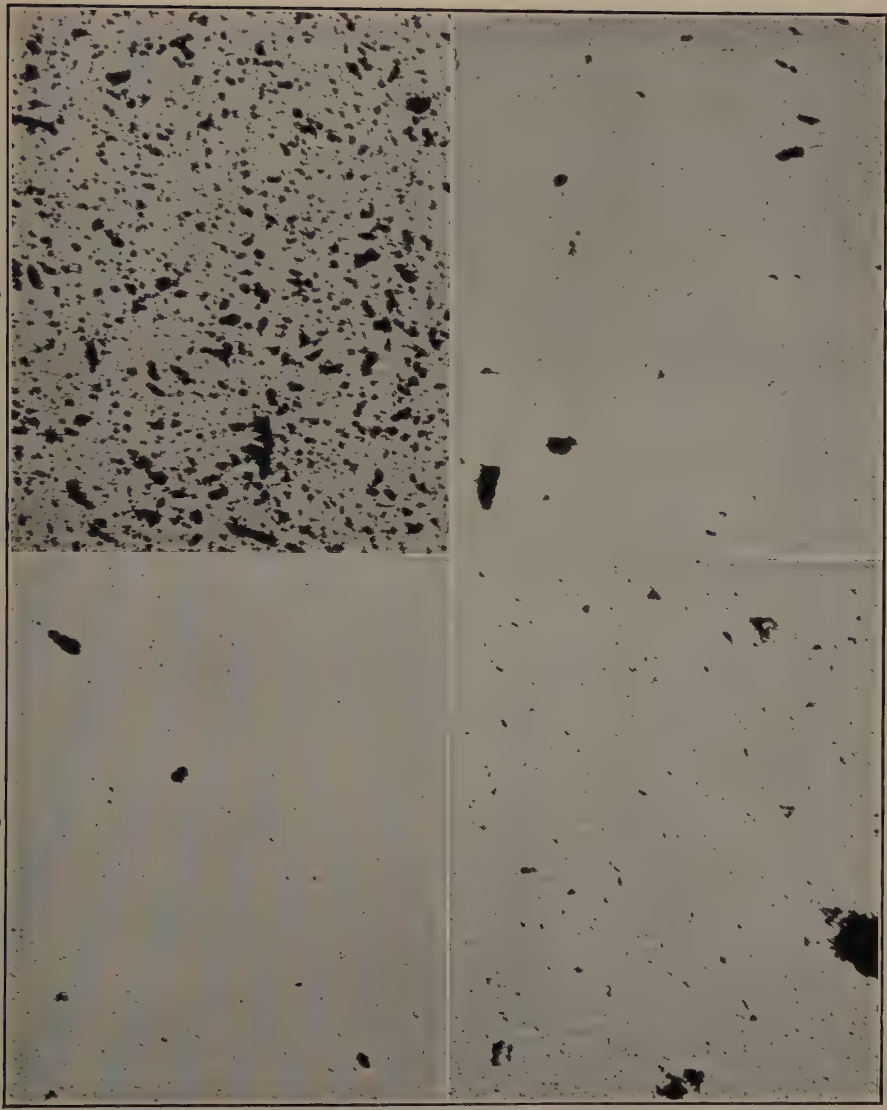

Fig. 8.—WC + 6 per cent Co.
Sintered 1350° C. Hardness, 86.5; density, 13.70; strength, 76,000 lb.
Fig. 9.—WC + 6 per cent Co.
Sintered 1425° C. Hardness, 91.2; density, 14.94; strength, 193,000 lb.
Fig. 10.—WC + 6 per cent Co.
Sintered 1500° C. Hardness, 91.0; density, 14.92; strength, 187,000 lb.
Fig. 11.—WC + 6 per cent Co.
Sintered 1575° C. Hardness, 90.5; density, 14.87; strength, 178,000 lb.
All × 200, unetched.

tungsten-carbon-cobalt, the absorption of carbon in excess of the amount necessary to satisfy the demands of WC is apparently very slow, and results in no positive changes in properties or structure. Loss of carbon, on the contrary, is readily recognized by the appearance of a low-carbon

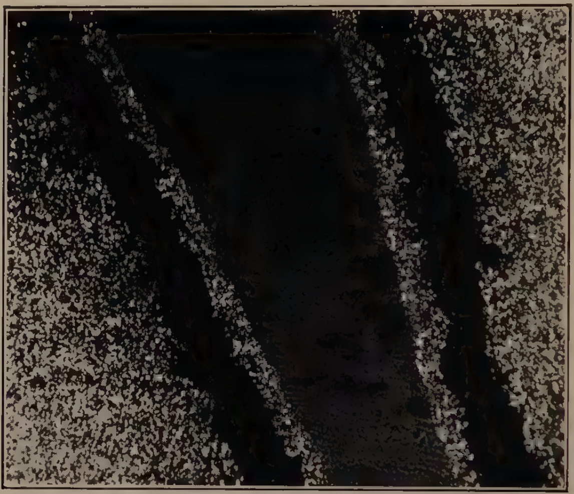

FIG. 12.—LARGE NONMETALLIC INCLUSION IN CEMENTED CARBIDE ALLOY. × 200.

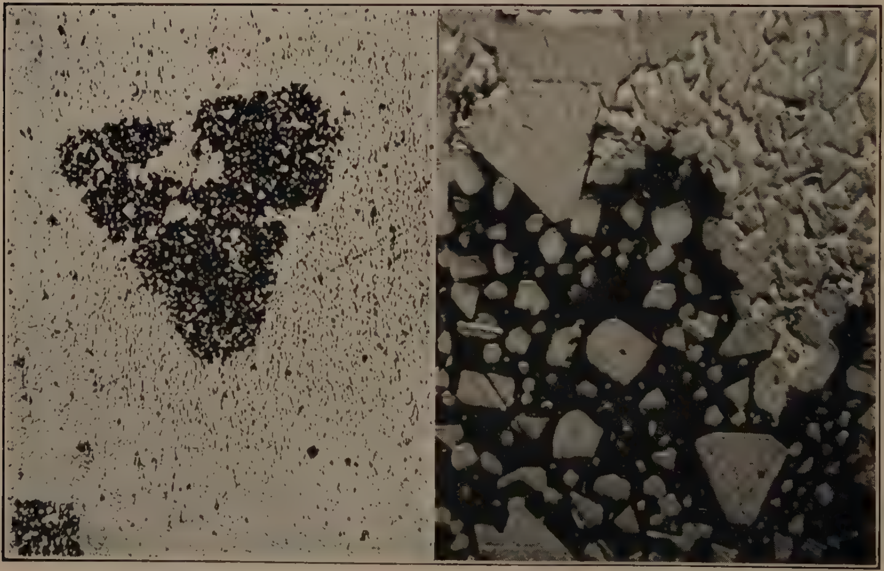

FIG. 13. FIG. 14.

FIG. 13.—DARK-ETCHING LOW-CARBON PHASE DEVELOPED BY DECARBURIZATION DURING SINTERING. × 200.

FIG. 14.—DARK-ETCHING DECARBURIZED AREA AT SURFACE OF CEMENTED CARBIDE ALLOY.

phase in the microstructure, which is rapidly darkened by the oxidizing action of the alkaline potassium ferricyanide solution, a standard etchant of WC-Co aggregates.

An exaggerated example of this low-carbon constituent is shown in Fig. 13. The symmetrical shape of the dark-etching constituent is one of its characteristics. A severe case of surface decarburization is illustrated by Fig. 14, where again the dark-etching constituent is forming at the expense of the angular WC crystals and the cobalt-rich cement, which appear in their normal form in the lighter portion of the field.

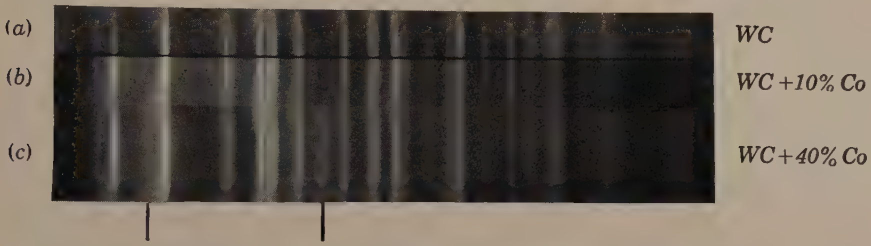

Fig. 15.—X-ray photograms of WC-Co alloys.

Methods of X-ray diffraction have been applied in a limited way to the analysis of structures appearing in the cemented carbide alloys. In the alloy under discussion, the identity of the dark-etching low-carbon constituent has been tentatively established from combination of metallographic and X-ray data.[2,3] It appears to represent a phase occurring in the pseudobinary system Co-W_2C, and seems to be associated with the hypothetical compound $W_2C\ (Co)_2$.

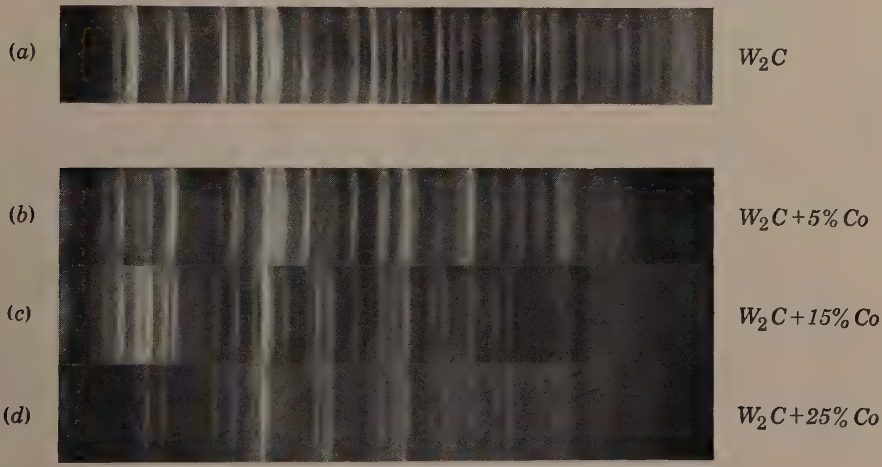

Fig. 16.—X-ray photograms of W_2C-Co alloys.

Reflections observed in X-ray photograms of any composition in the Co-WC series after sintering at 1450° C. are those belonging to the original components only, as may be seen from Fig. 15. Here two cobalt reflections are indicated below the photograms.

On the other hand, from a sintered alloy of W_2C and 5 per cent Co a new pattern appears, as shown in Fig. 16. When the cobalt content is increased to 15 per cent, a third set of lines is observed, which includes reflections from the phase $W_2C\ (Co)_2$ shown in the lower photogram. Takeda[3] has recently attributed the success of cobalt as a cementing material to the fact that cobalt and WC represent the stable solid phases in this alloy system.

A second example of a recognized structural change associated with altered composition is furnished by the tungsten carbide-cobalt alloy bearing iron in quantities approximating 0.5 per cent. This constituent, also darkened rapidly by the etchant, disappears after the alloy has been sintered in a carburizing atmosphere. The zone of increased carbon content is plainly shown by the etched section in Fig. 17 and at a higher magnification in Fig. 18, although the identity of the dark-etching constituent is unknown.

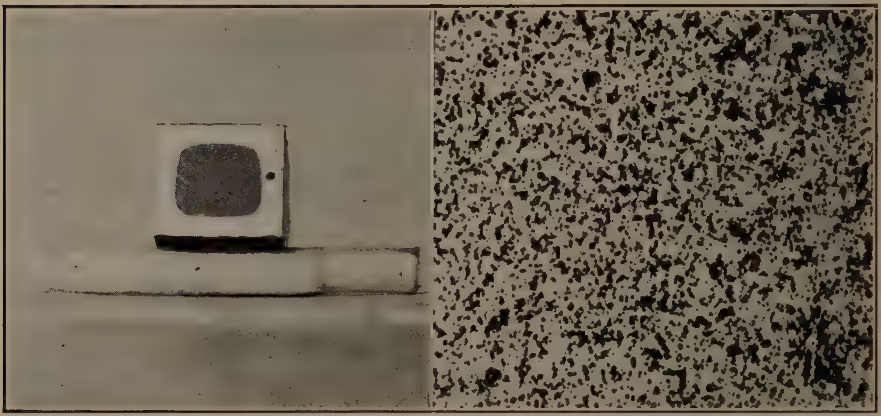

FIG. 17. FIG. 18.

FIGS. 17 AND 18.—WC + 6 PER CENT Co. CONTAINS 1.2 PER CENT Fe. SINTERED IN CARBURIZING ATMOSPHERE.
Fig. 17, × 2.
Fig. 18, field in unaltered core shown in Fig. 17, × 200.

The commercial success of a new alloy depends largely upon the judicious selection of its applications in the field of industry. While physical and mechanical properties may point the way to suitable uses, the final decision must be made from service records extending over long periods of time.

Upon the basis of such experience, the alloys of tungsten carbide and cobalt that have been described thus far fall into several classes of service, which are determined by the cobalt content, as might be expected. The 13 per cent Co grade is employed extensively in the form of large dies for drawing, extrusion, and shaping operations that demand a material of high strength. For smaller dies, and to a limited extent for cutting tools, a 9 per cent Co grade is used. In the field of cutting tools for machining cast irons, most nonferrous alloys and many nonmetallic substances, the 6 per cent Co alloy finds a wide variety of applications. In operations involving fine cuts at high speeds, a tool material containing as little as 3 per cent Co is often employed. In such service, the higher resistance to abrasion contributed by the tungsten carbide constituent in the tool may be profitably utilized, since no excessive demands are made upon its strength or resistance to shock.

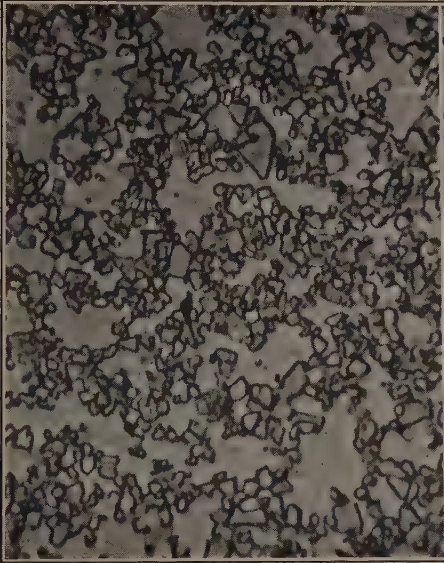

Fig. 19.

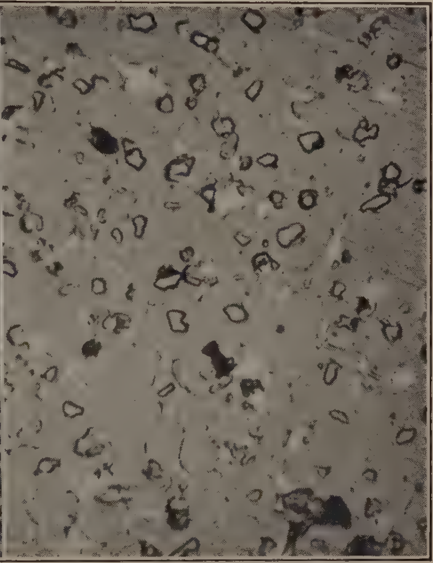

Fig. 20.

Fig. 19.—60 per cent WC, 27 per cent TaC, 13 per cent Co. Sintered 1450° C. × 1500.

Fig. 20.—61 per cent WC, 32 per cent TiC, 7 per cent Co. Sintered 1450° C. × 1500.

It will be observed that steel was omitted from the list of materials that can be profitably machined with tools of cemented tungsten carbide. The failure of tungsten carbide to cope with the cutting of steel appears to be associated with the higher cut pressures involved in such work, which lead to early failure of the tool by the phenomenon known as "cratering" or "loading." In this type of failure, fragments of the steel chip weld to the tool and break out small particles of the carbide alloy, in time causing the cutting edge to crumble.

Both tantalum carbide and titanium carbide resist this cratering action effectively, seemingly by lowering the coefficient of friction, and for this reason the tools best adapted for steel cutting contain the carbides of tantalum or titanium together with tungsten carbide and cobalt.

As intimated earlier, the microstructures exhibited by such combinations have by no means been completely interpreted, although they serve as effective controls in manufacturing a uniform product. As an example of mixed carbides, the structure of the alloy 60 per cent WC, 27 per cent TaC and 13 per cent Co after sintering at 1450° C. is shown in Fig. 19. Here the darker crystals are presumably WC while the TaC and Co have seemingly merged to form the lighter matrix. On the other hand, a mixture of 61 per cent WC, 32 per cent TiC and 7 per cent Co after sintering at 1450° C. yields the structure of Fig. 20. The cored nature of this pattern suggests at once a reaction, probably involving the two carbides as well as the cobalt and yielding as a product the constituent of intermediate shade that covers the greater portion of the field and occurs in rounded masses completely enclosing the small, light gray cores, which possibly represent a residue of WC. The discontinuous network of lightest shade would, under such interpretation, correspond to a cobalt-rich constituent.

From the fragmentary nature of the data presented may be judged the relatively meager store of metallurgical knowledge that has thus far accumulated in this field of the cemented carbides. In spite of this situation, however, alloys of this type have attained a real position in the commercial field, owing largely to the judicious application of the data collected during the course of the experimental work required to bring these alloys to their present stage of usefulness.

Acknowledgments

Many of the photomicrographs shown in this discussion were prepared by Finley H. Ellinger, while A. B. Gladding furnished the X-ray photograms. To George W. Lucas and Adam MacKenzie, I am indebted for details of the properties and applications of the alloys.

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DISCUSSION

(Samuel L. Hoyt presiding)

F. H. Clark,* New York, N. Y.—One use for tungsten carbide that is not generally known is its application for electrical contacts for mechanical relays. Formerly, the

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* Metallurgist, Western Union Telegraph Co.

Western Union Telegraph Co. utilized an electrical contact of a platinum-iridium alloy. At the 60 Hudson Street building in New York, seven men were required just to clean contacts, as some of the contacts on relays for press circuits had to be burnished three times a day. The substitution of tungsten carbide bound with cobalt increased the life of the contact to as much as two years. This alloy is satisfactory for operation on relays where the current is less than one ampere, the voltage about 160 and under service conditions of light pressures and high speeds. In service, the tungsten carbide contact does not build up a "cup" and "cone" on the surfaces but wears down flat, and a very small amount of fine powder collects below the contact. It may be that this effect is due to the fact that the material is a sintered product.

E. M. Wise,* Bayonne, N. J.—I should like to ask Miss Clark whether she would care to add anything concerning the later developments of the tungsten.

F. H. Clark.—Tungsten carbide bound with certain noble metals, notably osmium, has given long life as a relay contact. We have experimented with tungsten boride bound with a series of different metals. One particular boride combination continued to operate indefinitely, but we could never duplicate it. We have also had successful operation with a platinum-tungsten alloy but had some difficulty in duplicating our results, owing perhaps to lack of uniformity of the tungsten.

G. Sachs,† Newark, N. J.—When sintered tungsten carbide came to commercial application, there were two processes used: sintering without pressure and sintering under pressure. I wonder which process is mainly used today in manufacturing these alloys?

W. P. Sykes.—The so-called cold press is generally used. It is pressed cold and heated afterwards, although in certain plants the hot-press method is still used for forming certain shapes.

G. Sachs.—As I remember, there were quite distinct differences in the property of these two types of alloys.

W. P. Sykes.—There still is some difference, but it has never been very certainly established as to how consistently the products differ; that is, they sometimes appear to have decidedly different characteristics, and at other times there does not seem to be much difference. As a matter of fact, that is still under investigation from a production standpoint.

F. M. Walters, Jr.,‡ Youngstown, Ohio.—Does the binder of cobalt dissolve the tungsten carbide to any extent in the sintering process and is it precipitated on the range as put into the mix or in a new range for it?

W. P. Sykes.—That question has been asked for years. So far as I know, cobalt does dissolve some of the tungsten carbide, for the equilibrium diagram for the binary system of cobalt and tungsten carbide does show that the cobalt dissolves up to 15 per cent of the tungsten carbide at the solidus temperature; below that temperature, the solubility drops off, but that is under equilibrium conditions. In the sintering process we do not know how nearly that equilibrium condition is approached.

S. L. Hoyt,§ Milwaukee, Wis.—I believe you said that a slight excess of carbon over the WC ratio was all right. With a carbon content below the WC ratio, loss of strength develops. As I recall it, the carbon can go up to 7 per cent in the WC mixture and still get good results in the finished product if the cobalt content is not too high, and if the sintering temperature is increased accordingly. In other words, you would sinter at about 1600° C. with 7 per cent C, whereas with 6.1 per cent C the sintering temperature would be at 1500° or less for that cobalt content. Have you ever done anything along that line? As far as I know, there is no particular advantage in having a higher carbon content.

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‡ Research Engineer, Youngstown Sheet and Tube Co.

§ Research Metallurgist, A. O. Smith Corporation.

G. J. Comstock,* Bridgeport, Conn.—What was the over-all composition of the matrix?

W. P. Sykes.—I do not know. The first thing I should do would be to obtain a diffraction pattern from it. I think that this is in the mill at the present time, but it had not come out when I left Cleveland.

G. J. Comstock.—The structural form would indicate the possibility of an alloy between cobalt and tantalum carbide.

W. P. Sykes.—I should not be surprised if that were the case.

G. J. Comstock.—In the higher tantalum combinations, that is when further amounts of tantalum carbide are added, the structural change you obtained is pronounced; that is the difference between the structure shown when the tantalum carbide present was on the order of 27 per cent, and when the tantalum carbide was present in larger proportion. The structural forms shown were markedly different, and the lower proportion of tantalum carbide unmistakably suggests an alloy that has been formed between tantalum carbide and cobalt.

C. Hardy,† New York, N. Y.—Have you determined how much of the carbon you lose during the hydrogen treatment, expressed by percentage? Do you know whether you lose a great deal more when you reach 1450° or 1500° or whether you get at the start all the losses you will have? You told us you put in a carbon tube to replace the carbon that is lost. Now, if you start with a certain percentage of carbon, how much carbon do you expect to lose that you have to replace?

W. P. Sykes.—Mr. Hardy's question has to do with the loss of carbon during the sintering operation, and whether arrangements are made to replace it—or, to put it in other words, whether the loss of carbon is compensated by some special atmosphere, or by the carbon tube in which the sintering operation is performed. I should prefer to think of it in this way: that the carbon is introduced into the furnace atmosphere from the carbon tube surrounding the work, not to replace the carbon that is lost, but rather to make an atmosphere that is relatively rich in carbon. If any change takes place, it would result in an increase of carbon in the alloy.

C. Hardy.—We have that problem when we try to make steel with a given carbon content. As we reach the higher temperatures, we lose at least half our carbon. We are figuring with 0.25 or 0.30 carbon, and in the hydrogen furnace we lose a great deal of that.

W. P. Sykes.—I suppose that is because of a change in equilibrium relationships between carbon and one of the hydrocarbons in the furnace atmosphere as the temperature changes.

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† Charles Hardy, Inc.

S. C. Spalding,* Waterbury, Conn.—Is it feasible to make satisfactory products of reclaimed carbide, or is it necessary to always use virgin materials? Does it make any difference in the carbide that might be made in that way?

W. P. Sykes.—We do use reclaimed carbide for some products. I do not know whether there is a great deal of difference in quality between virgin carbide and the reclaimed carbide.

A. F. Braid,† New York, N. Y.—I do not know much about the sintering process, but in view of the lower price of titanium I should like to know why more titanium is not used?

W. P. Sykes.—As nearly as I can say, it is because more titanium would not be quite as good as the amount we use; that is, the compositions are determined by trial and error, and the composition is finally determined by the one that seems to do the best work.

G. Sachs.—From the theoretical point of view, it may be interesting to know that tungsten carbide is extremely plastic at temperatures above 2500°. I wonder whether this means that this temperature or a somewhat higher one limits the application of tungsten carbide. Some years ago we experimented with tungsten carbide, pure and with the addition of cobalt. We found that by using sufficiently high temperatures we were able to bend, compress, or press rods of these alloys into any shape desired. At sufficiently high temperatures the tungsten carbide is extremely soft and plastic.

E. E. Thum,‡ Cleveland, Ohio.—The tungsten carbide problem is only one phase of a rather large problem of hard cutting materials. Miss Clark mentioned the borides. Materials of a cognate nature formed in a variety of ways have been used for a long time as substitutes for industrial diamonds in well drilling and other processes requiring extreme resistance to abrasion. Theoretical treatment of these alloy systems is still practically nonexistent, but I do believe that the future will see a large extension of hard materials of this general nature.

W. P. Sykes.—I have very little to say in reply to all these remarks. It is undoubtedly true that the presence of cobalt in a steel, for instance, contributes markedly to the so-called red-hardness of the material, because we have data from tests that show that the red-hardness, i.e., the hardness at temperatures of 600°, 700°, 800° C., increases very regularly with the increase in cobalt content.

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Tantalum Carbide Tool Compositions

By Philip M. McKenna,* Member A.I.M.E.

(New York Meeting, February, 1938)

When a new material becomes available to industry, it is useful to describe its properties as a guide to its most effective application; and when the new material may be produced in compositions having a series of graded properties, tests to select the combination of properties best adapted for various uses are helpful. The class of materials to be considered in this paper are hard tool materials produced by processes of powder metallurgy from hard carbide constituents and various matrices of iron, nickel or cobalt, or alloys of them with tungsten, or tungsten and carbon.

The customary use of carbide hard alloys is for metal-cutting tools; although wire-drawing dies, lathe centers, follow rests, grinding rests, burnishers, rolls, extrusion dies, measuring gauges and micrometers, and a number of other tools are also made with these hard alloys as the essential wear-resisting parts. The properties and tests to be considered are those affecting these uses.

In the development of tool materials since the industrial revolution we have had carbon tool steels, Mushet steel, high-speed steels, stellites, and now cemented carbide compositions. For an understanding of the latter category of materials their properties and uses relative to the older and more familiar tool materials will be considered.

Hardness has been the property of greatest practical interest in tool materials. The word "hardness" is a generalized term lacking definiteness unless the specific test used is described. However, efforts to explain physical properties as a consequence of chemical bond, and distance between atoms in chemical compounds have been illuminating. This seems the most generalized attack on the problem, and is based upon the idea that atoms in a lattice are held together as the square of the valence and inversely as the square of the distance between the atoms. The compounds compared must all be of the same crystalline arrangement. It is interesting to note the values of the figure $\frac{100W^2}{V_A^{2/3}}$ for a number of

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Manuscript received at the office of the Institute Dec. 10, 1937.

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chemical compounds of the same atomic crystalline form as tantalum carbide as given in Table 1.

Such figures fail to take into consideration the possibility of a mosaic structure, or grosser defects in the crystalline lattice permitting breakage at places less strong than the atomic bond. Nevertheless, it is interesting that the rank of hardness by such tests as Mohs' scratch hardness are consistent with the rank of the figures obtained by calculation. Hardness defined as volume compressibility per unit load is also an attempt at generalization, and such work as has been done at the Bridgman laboratories for many substances is fundamental. However, we are not aware that compressibilities of the carbides used in hard alloy compositions have been observed, either in their pure state or cemented into the hard alloys used for tools. Compressibility is doubtless very low in these hard substances.

TESTS

Hardness.—As a practical matter, tool materials today are tested for hardness by the familiar Rockwell testing machine, the C scale with 150-kg. load being used for tool steels and stellites, while the A scale with the 60-kg. load is generally used for testing hard alloys, although the 45N scale is also used with the superficial hardness Rockwell machine. For the approximate conversion of the C-scale figures to A-scale figures, either the formula

$$Rc = 2R_A - 104$$

TABLE 1.—*Figures Obtained by Considering the Valence Squared Divided by the Atomic Volume to the Two-thirds Power in a Series of Compounds of Sodium-chloride Type Crystalline Arrangement*

Compound[a]	NaCl	AgCl	NaF	PbS	CaO	MgO	TiN	ScN	VN	CbN	TiC	ZrC	HfC	VC	CbC	TaC
Valence..........	1	1	1	2	2	2	3	3	3	3	4	4	4	4	4	4
Density..........	2.2	5.56	2.83	7.42	3.37	3.65	5.18	4.46	5.63	8.40	4.25	6.90	12.20	5.36	7.82	14.47
Lattice *a*..........	5.628	5.54	4.62	5.97	4.79	4.20	4.40	4.44	4.28	4.41	4.60	4.76		4.30	4.46	4.445
Atomic vol..........	13.53	12.8	7.42	16.1	8.39	5.57	6.17	6.65	5.77	6.42	7.05	7.48	7.81	5.87	6.708	6.67
$100 \times \frac{W^2}{V_A^{2/3}}$*......	18	19	26	63	97	127	268	255	280	260	435	418	406	491	450	452

[a] These compounds are all of the same crystalline form—NaCl type cubic. The distance *a* is the number of Ångström units between similar kinds of atoms.

* W = valence; V_A = atomic volume = atomic weight/density.

or the reverse

$$R_A = \frac{R_c}{2} + 52$$

has been suggested.

A clue to differences in flow of the carbide compositions when tested by a diamond point pressed into the metals is given by the graph in Fig. 1. The compositions that contain a high percentage of tungsten carbide with a low percentage of tantalum carbide and a cobalt matrix constituting less than 15 per cent of binder, when tested by both the C and A scales, follow the straight-line formula indicated; but the more ductile compositions comprising a large percentage of tungsten alloy binder, up to 30 per cent, and a high percentage of tantalum carbide or equivalent carbides read lower on the C scale than the calculated figure obtained from the A-scale observation. The reason for this is that under the heavier C-scale load the more ductile compositions and the more rigid compositions yield in different ways.

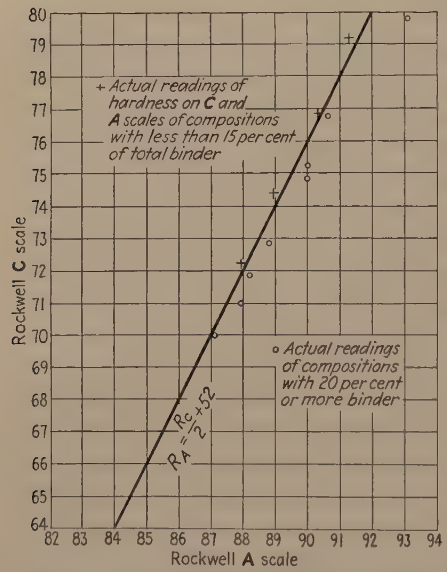

FIG. 1.—FLOW OF CARBIDE COMPOSITIONS TESTED BY DIAMOND POINT PRESSED INTO METAL.

Readings with high binder content are all on right-hand side of conversion formula.

Strength.—Strength of hard alloy compositions is observed by a transverse rupture test of equal importance to the Rockwell test. In this test a rectangular bar of the hard alloy 0.200 in. thick by 0.375 in. wide, supported between $\frac{9}{16}$-in. line centers, is broken by the application of a load (kilograms) in the center, the weight of the load when the bar breaks being observed. By beam formulas this is arbitrarily reported as "pounds per square inch on transverse rupture" by multiplying by 124. This is correct only if it is assumed that the tensile strength is equal to the compressive strength and the neutral axis is at the geometric center of the bar. Since this is probably not true, the test is an arbitrary one, although of great practical value.

Elasticity.—The modulus of elasticity has been observed in tungsten carbide compositions with 13 per cent cobalt bond to be 79,000,000 lb. per sq. in. and in tantalum carbide compositions with a much greater quantity of bond of a different nature, 56,000,000 lb. per sq. in.[1] It is significant that the elastic limit of carbide compositions with high percentages of alloy binders is about 2.4 times that of tungsten carbide compositions with cobalt in low percentage, and it takes more work to break it although it is less rigid. For use in steel cutting, hard alloys must resist breakage, as well as have the desired hardness. A test measuring the modulus of elasticity consists in utilizing the Rockwell machine for applying a load and measuring the distance of flexure of a beam of hard alloy 0.125 in. thick by 0.150 in. wide supported between 1-in. centers, and pressed in the middle with a hardened steel ram of ⅛-in. radius. Each mark on the Rockwell C scale represents a movement of 2 microns, or 0.002 mm. The idle load is 6.6 kg. and the flexure caused by the addition of 100 kg. is the measurement observed. Some observations of flexure with materials of different compositions are contained in Table 2.

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[1] Metals Handbook, 1936.

TABLE 2.—*Flexure with Materials of Different Compositions*

Symbol	Binder, Per Cent	Break, Kg.	Rockwell A Hardness	Flexure with 100-kg. Load		Remarks
				Marks on C Scale	Microns	
388	4+	1530	91.8	22.5	45	Co + W + C bond
1	5+	1540	91.8	22.5	45	Co + W + C bond
4473	5+	1740	90.0	23.	46	Ni + W + C bond
2	8+	2160	89.0	31.	62	Ni + W bond
4	23	1600	91.6	37.	74	Alloy Co·W-C bond
4473	27	1800	91.0	38.	76	Ni:W alloy bond
420	27	2410	88.	34.	68	Ni + W bond
HSS		4100	85.0	67.0	134	Hardened 18-4-1 HSS

Thermal Conductivity.—Another fundamental property of tool materials is thermal conductivity. This property varies widely in hard alloys, from about 0.18 to 0.043 cal. per cm. per deg. C. per sec. For steel-cutting tools it seems essential that the tool materials have a certain resistance to the flow of heat; in other words, a lower thermal conductivity than in the grades used for cutting cast iron. The reasons for this seem to reside in heat distribution between the tool and chip during fast cutting. In cutting cast iron, or materials with a crumbly or powdered chip, the work is done close to or at the cutting edge, where frictional heat may be generated to an extent that may soften the binder matrix and permit the wiping away of the carbide particles—therefore a material conducting heat away more rapidly from the small volume of the immediate vicinity of the cutting edge may be run at higher speed on this class of work. When operating on tougher metals, such as malleable iron, certain tougher cast irons, and steels, the chips are formed and removed in a different manner, being split off with the area of contact between the tool point and chip somewhat back of the edge. This area of the tool point must resist the "cratering" action of the hot, rapidly moving metal chip. Tool compositions containing high percentage of tantalum carbide, or similar carbides other than tungsten carbide, resist "cratering" of this nature and they also have greater resistance to the flow of heat. An optimum heat conductivity for a steel-cutting tool material seems to be about 0.065 cal. per cm. per deg. C. per sec., which, incidentally, is almost exactly that of high-speed steel in the hardened and drawn condition.[2] For special purposes such as fast precision boring the desirable thermal conductivity may be even lower.

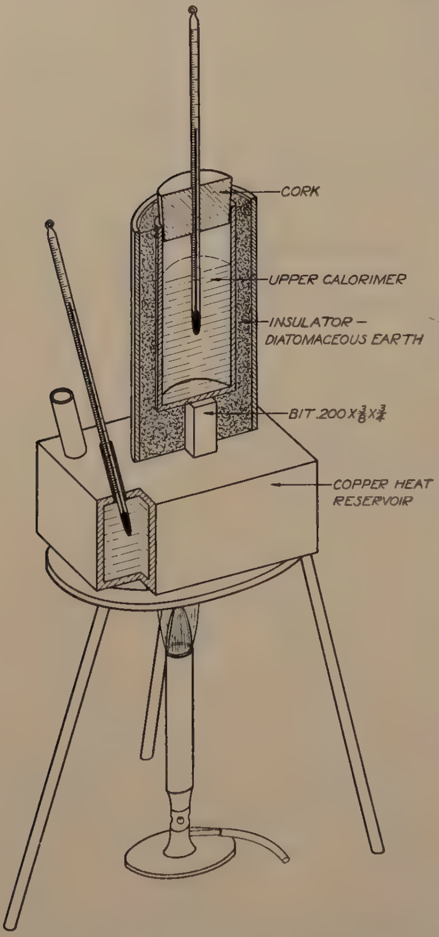

FIG. 2.—APPARATUS FOR TESTING THERMAL CONDUCTIVITY.

A means used to test thermal conductivity is the apparatus shown in Fig. 2. It is admitted that the test is restricted to a range between room temperature and the boiling point of water, and that the results may not be absolute; nevertheless, this method gives consistently reproducible comparative results and may be rapidly conducted without destruction of the specimens, which are of economical size. Results observed by this means, checking heat losses in the apparatus by using standard materials, particularly pure lead, are shown in Table 3.

The specimen to be measured for thermal conductivity is brazed on the ends with naval brass and a flux. This is ground off very thin and flat and the specimen soldered with soft solder between the upper and lower heat reservoirs. The insulation is placed around the specimen in a cardboard retainer. Water about 90° C. is placed in the lower vessel and a measured amount of water in the upper calorimeter at room temperature. Temperatures are observed at one-minute intervals over a period of 12 min. The potential difference in degrees Centigrade over these one-minute intervals between the upper and lower vessels is observed, and used in the calculations, but practice enables the operator to manipulate the burner to maintain an approximately equal potential difference, so that the increments are lineal and may be averaged over the 12-min. interval. The dimensions of the bit are taken into consideration as in measurements of electrical conductivity. Agitation may be effected by a separate stirrer in the upper vessel (not shown).

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[2] D. Hattori: *Jnl.* Iron and Steel Inst. (1934) **129**, 289–309.

Microscopic Examination.—Another test is by microscopic examination. Owing to the very fine grain size of good hard alloys produced by methods of powder metallurgy, higher magnifications are necessary than with steels or melted alloys to distinguish constituents. The hardness of the materials requires very careful lapping with the finest diamond dust to obtain plane surfaces in focus. Etching is done on tantalum carbide alloys with solutions of potassium hydroxide plus potassium ferricyanide, the more rapid etchant of a mixture of hydrofluoric acid plus nitric acid being too severe. At 1500 magnifications most of the grains apparent by such etching in a good hard alloy composition are about 2 mm. across, representing a grain size of about 1.3 microns. Exact interpretation of these photomicrographs is difficult at present.

TABLE 3.—*Thermal Conductivity of Hard Tool Materials*

Designation	Thermal Conductivity, Cal. per Cm. per Deg. C. per Sec.	Applications and Remarks
76	0.199	WC:Co composition. Very good on light cuts on C.I.
6083	0.185	C.I. cutting at high speeds. WC:Co composition.
6021	0.141	C.I. cutting below 300 ft. per min. WC:TaC 3% Co.
5483	0.140	C.I. cutting below 300 ft. per min. WC:TaC 4% Co.
5405	0.108	Malleable iron and steel castings. WC:W-Ni bond.
5109	0.0912	Malleable iron and alloy iron. WC:TiC:TaC Co.
5403	0.086	Steel-cutting tool. Less enduring than same composition with lower conductivity.
WXX	0.084	Steel-cutting grade of TiC:WC:Co. Too high in conductivity.
5299	0.065	Steel-cutting tool. Better than 5403 because of lower conductivity.
5037	0.0645	Excellent steel-cutting tool at high speeds (above 400 ft. per min.).
5157	0.0685	Excellent steel-cutting tool for rough work.
423	0.0532	Good steel-cutting tool when coolant is avoided.
1919	0.0562	Soft roughing grade of tantalum carbide with Ni:W bond.
HSS	0.0612	18-4-1 HSS as cast.
HSS	0.0611	Quenched and drawn 18-4-1 HSS.
HSS	0.0551	Quenched 18-4-1 HSS.
HSS	0.0683	Quenched and drawn 18-4-1 HSS.
44	0.043	Steel-cutting tool of Ta, Cb and Ti carbides used for fast precision boring of steel at speeds up to 800 ft. per min.

Desirable Properties

Tantalum carbide as previously prepared by the carburization of tantalum metal, or by heating tantalum oxide with carbon, approached, but never equaled the monatomic ratio of carbon to tantalum of 6.22 per cent C in the carbide, nor did it have the density of 14.48, of macrocrystalline TaC produced under a menstruum metal. A menstruum metal is one dissolving both carbon and tantalum, permitting the formation of TaC from these atoms in the liquid phase. For instance, the density of tantalum-carbon materials described as TaC was thought to be 13.95 to 14.05.[3] Examination of these carburized substances containing tantalum and carbon always showed that they were mechanically separable, as by "panning" with liquids, into a small amount of free carbon and a material comprising less than 6.224 per cent C. If more carbon than 6.224 per cent was present in the substance, as by admixing with carbon and heating, even repeatedly, the excess carbon was always removable by mechanical means, leaving a substance lower than 6.22 per cent C. For some time it was suspected that a compound Ta_6C_5 existed,[4] but the evidence seems inconclusive.

The importance of this from the standpoint of powder metallurgy of TaC compositions was that a small deficiency of carbon in the TaC resulted in lower break strength in the composition. It is significant that free tantalum in the alloy matrix does the same thing, and is greatly to be avoided, as the utility of tool materials depends upon a desirable combination of strength and hardness. Also, a higher ratio of tungsten to cobalt or nickel in the matrix alloy is desirable because of its stiffness at elevated temperatures, and when free tantalum is picked up in this alloy it is rendered brittle, whereas when TaC prepared under a menstruum metal is employed the high percentage of tungsten in the matrix may be used with concomitant high break strength and resistance to deformation at tool temperatures when cutting.

Without a means of comparison of tool compositions having different strengths and hardnesses, it was necessary to compare composition of identical percentages of binder to carbide present, which was not always convenient. To meet the need for a method of comparison the following tool value formula was found useful:

$$\text{Tool value} = \frac{10 \times \text{break strength in kilograms}}{5(93 - R_A)\left(47 - \frac{R_A}{2}\right) + 140}$$

This formula is based on the idea that a par combination of strength and hardness is 1400 kg. on break test and 93 Rockwell A. To maintain par when the hardness is decreased, strength must also be increased in accordance with the formula. Combinations that give 100 as a hardness strength are given in Table 4.

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[3] K. Becker: Hockschmelzende Hartstoffe und ihre technische anwendung, 52.

[4] M. Andrews: *Jnl.* Amer. Chem. Soc. (1932) **54**, 1845.

Tool performance depends upon the physical and chemical properties of the tool material under the conditions of work. To consider the various properties required for tool materials for different kinds of work, the following results obtained by practical experience will show how the tests for hardness, strength, thermal conductivity, microstructure and chemical composition are applied. The tool-value formula suggested is of use only in comparing compositions otherwise of the same general natures, and is not to be considered as comparing widely different compositions.

How hard should the tool material be? The answer is, the harder the better if it does not break. Commercial tool materials of hard carbides vary from 85 to 93 Rockwell A.

TABLE 4.—*Combinations That Give Hardness Strength of One Hundred*

Rockwell C	Rockwell A	Break Test on Standard Piece, Kg.
	94	1375
	93	1400
	92	1450
	91	1550
	90	1700
74	89	1900
72	88	2150
70	87	2450
68	86	2800
66	85	3200
64	84	3650
62	83	4140

How strong must it be? This is like the question, how long should a man's legs be? The tool material should be strong enough to do the work required without breaking. For machining Bakelite, hard rubber, green porcelain, Transite, glass and other weaker abrasive materials with a powdered chip, most hard carbides are strong enough if over 1000 kg. in the break test. For machining cast iron, brass and silicon-aluminum alloys producing granulated chips, a little more strength is essential, and about 1300 kg. is the lower limit. For cutting improved irons above 40,000 lb. per sq. in. tensile strength, such as nickel iron, cast iron, copper-silicon alloy iron, malleable iron, and semisteel, considerable strength is needed, and tool materials above 1600-kg. strength are used. For intermittent cutting on cast irons and soft steels strength above 2000 kg. is needed. For cutting steels, as in the continuous turning of low-carbon steel of 200 to 250 Brinell, a strength above 1500 kg. is required, but for alloy steels from 250 to 400 Brinell the tool material should have a strength above 1700 kg. For intermittent cutting on cast steels, often having blowholes, a strength above 2000 kg. is necessary, and tool materials with a high percentage of bonding alloy are used with strengths above 2200 kg. For intermittent and rough cutting these materials with a high percentage of bonding alloy for the carbide crystals have the lower rigidity as described under the test for modulus of elasticity. These meet shocks better because they may be bent further within the elastic limit.

What should the thermal conductivity be? For light cuts on cast iron at speeds at which the frictional heat at the extreme edge of the tool approaches 1500° F., which is about 400 ft. per min. peripheral speed, the higher thermal conductivity of tungsten-carbon-cobalt compositions gives the better results. This is because the edge operates at a cooler temperature when the tool material is a better conductor. The difference between 0.18 and 0.14 thermal conductivity is noticeable in tool wear at these speeds, because the tool with the lower conductivity gets hotter at the edge, permitting the wiping away of carbide particles from the matrix softened by frictional heat. For heavier cuts on cast iron this factor is not important, as the speeds are necessarily lower, on account of limitations of the machines, and a tool material that is stronger, and of a chemical nature resisting cratering, is best suited because it does not crumble on the "scale line," or other rough places on castings. Tool materials of high thermal conductivity, such as tungsten carbide cemented with cobalt, are unsatisfactory for cutting materials such as steel with long, tough chips, for they crater many times more rapidly than the special tool-cutting compositions containing tantalum carbide, or those containing titanium carbide. The German Widia N for cutting cast iron has a conductivity of 0.19 while the tool material recommended abroad, containing 16 per cent TiC, known as XX, has a conductivity of 0.09. The latter composition still does not equal in performance the compositions widely used in America for steel cutting and having a conductivity of 0.0645. For very fast light cutting in precision boring of steel, a tool material high in tantalum carbide, with a thermal conductivity of 0.043, is widely used. Another factor to be considered is the effect of thermal conductivity on grinding, for with silicon-carbide wheels heat-checking of tool materials of lower thermal conductivity takes place more readily. However, diamond-impregnated Bakelite wheels eliminate this problem for any conductivity.

What should the microstructure be? It depends on the nature of the work. For drawing dies, it is essential that there be no porosity, and the photomicrograph will disclose pores, which cause pickup in drawing soft wires. Other things being equal, the smaller average grain size with a certain proportion of variety of size makes a better tool material. Photomicrographs with ordinary light do not show the ultimate constituents in the bond. Perhaps work with ultraviolet light will reveal this.

As to chemical composition, an ultimate analysis for the elements contained is inadequate to guide the selection of these hard compositions for different uses, as the combination in molecular constituents may be different in tool compositions of the identical ultimate chemical composition. Analysis must be considered in view of the molecular ingredients put into the tool material. Insight into this is gained by tests of thermal conductivity and rigidity.

The ultimate test is the use of the material as guided by experience. Hundreds of tests have been run on actual jobs, of which a few instances may be given in closing.

In the machining of car axles to be mounted by press fits, it is desirable to have a smooth, accurate surface free from torn tool marks. With lathe tools tipped with the steel-cutting grade of cemented carbide having a strength of 1750 kg. (217,000 lb. per sq. in.), a hardness of 92.0 Rockwell A, a thermal conductivity of 0.0645, a fine grain structure, and a chemical composition containing tantalum and titanium as well as tungsten, cobalt and carbon, in a preferred combination, this work was done in 5 hr. floor to floor time, compared to 14 hr. with high-speed steel tools. The finish produced at the higher speed was excellent for pressed fits. The axles were of SAE 2340 alloy steel heat-treated to 250 to 260 Brinell. The tools were of 1 by 1½ by 10-in. steel shanks having carbide tips ⅜ by ½ by ⅞ in. The rough turning was done at 170 ft. per min. peripheral speed, 0.018-in. feed, and ¼ in. depth of cut, three shafts being obtained per grind of the tool. Finishing was done at 240 ft. per min., 0.015 in. feed and 1⁄16 to ⅛ in. depth of cut, the tool being reground every seven pieces.

Locomotive tires of a steel containing 0.65 C, 0.85 Mn and 0.35 Si are bored with similar carbide-tipped tools for the same reason; namely, to obtain the smooth machined surface, avoiding the starting of fatigue cracks in the tire when shrunk onto the wheel and subjected to use.

APPLICATIONS

To the metallurgical testing laboratory these steel-cutting carbide tools have been a boon for the machining of tensile-test specimens of heat-treated steels. On one occasion a specimen of steel that Rockwelled 67 C was turned on a lathe with one of these carbide tools.

What is known as "graphitized" steel is used for cylinder linings of Diesel engines, and affords an example of the way the tool material should be selected with reference to its properties for best results. The graphitized steel cuts with shorter chips than steel, and longer than crumbly cast-iron chips. Consequently, the tool point encounters both wear on the extreme edge and cratering back of the edge. It was found that the best tool for this work was of intermediate thermal conductivity; namely, about 0.080 cal. per cm. per deg. C. per sec. Its strength was 2100 kg. (240,000 lb. per sq. in.), its hardness 90.0 Rockwell A, and its composition comprised sufficient tantalum carbide to resist the cratering action. At a speed of 300 ft. per min., 0.018-in. feed and 1/16 to 1/8 in. depth of cut, tools tipped with this material produced 75 sleeves per grind of the tool, while a tool material of equal hardness but of 0.043 thermal conductivity produced only 10 pieces per grind. On the other hand, a grade of high thermal conductivity, 0.145, produced only 12 pieces per grind. Thus there is a certain combination of properties required in tool materials for different kinds of materials to be machined.

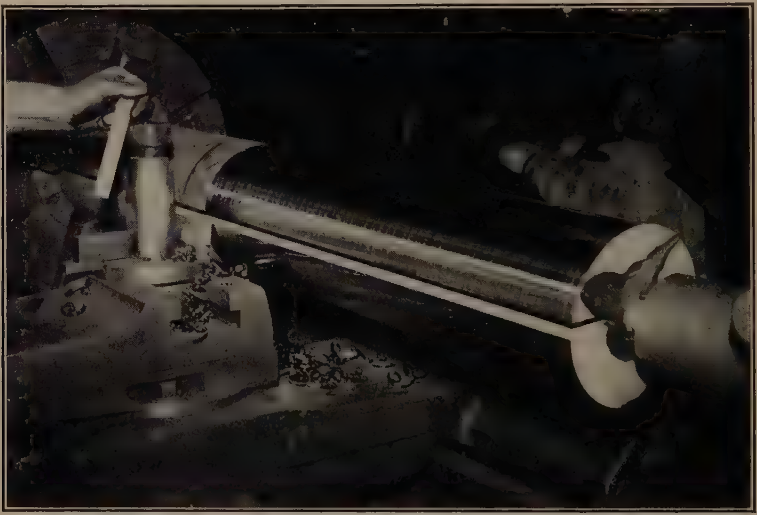

Fig. 3.—Turning an 8-inch bar of heat-treated chrome-vanadium steel.

A full description of the range of work done with carbide tools and the preferred properties for each job cannot be adequately treated in this article. The rugged service to which carbide tools of the high strength recently attained may be put is shown by the accompanying photograph (Fig. 3) of work done in turning an 8-in. bar of heat-treated chrome-vanadium steel, 364 Brinell, with a 3/4-in. slot. Turned at 75 r.p.m., or 152 ft. per min., the tool struck this hard steel 75 times a minute. The edge was ground flat on top, a 1/16-in. depth of cut and 1/32-in. feed were used. The bar was finished accurately and the tool did not fail by chipping during the work. This is attributed to the high break strength of 2210 kg. (275,000 lb. per sq. in.) and hardness of 90.5 with thermal conductivity suitable for steel cutting of 0.069 cal. per cm. per deg. C. per second.

Powder metallurgy has thus provided the engineering world with tool materials of great value in mechanical work, extending the range of materials that may be used in construction of durable steels and other metals previously avoided because of the difficulty of machining them commercially. The purpose of this paper is to describe the properties of the tool materials with a view to their selection for different classes of work.

DISCUSSION

(*Samuel L. Hoyt presiding*)

MEMBER.—What results are obtained when the sintering at the higher temperature is carried out in an atmosphere of hydrocarbons instead of hydrogen?

The next question is concerned with the thermal strains developed within these cemented mixtures. Under friction, where these carbide grains come into contact with the work, heat is developed at the point of contact. The number of British thermal units developed at the point of contact will vary, of course, with the friction, speed and other conditions, and perhaps some of these failures, such as crumbling, might be related to some extent to the flow of heat from that point through the grain, and then through the matrix, into the matrix and out of the matrix, developing a number of thermal strains.

P. M. MCKENNA.—We have found that tantalum carbide cannot be sintered with cobalt alone and produce a useful composition. I believe that it is associated with the question that was asked. The materials in successful use all comprise a matrix high in tungsten, and I regard that as very important, so that the thermal characteristics of the binder will be more like the carbide, especially for steel-cutting purposes. The coefficients of thermal expansion of the matrix containing high percentages of tungsten approach those of hard carbide constituents which are low, and I believe that is important.

P. T. WETTER,* New York, N. Y.—In cutting of steel, we have a higher conducting material than when cutting cast iron. The work piece will carry off the heat, leaving less heat to affect the tool tip and go back into the tool shank. How does this affect the composition and cutting edge?

Have you any figures on American costs of making titanium, tungsten and tantalum carbides?

P. M. MCKENNA.—The cost of the constituents has practically nothing to do with the cost of making hard carbides. It is true that titanium oxide can be bought for, I believe, about $40 a ton, but it is very immaterial at present.

P. T. WETTER.—Europe, particularly Germany, cuts without coolant. What advantage has this in economy of cutting steel?

H. H. LESTER,† Watertown, Mass.—Is it not true that the cemented carbide tools have less tendency toward forming the built-up edge? Is the absence of the built-up edge due to the fine finish or is it due to other properties of the tool? For instance, has the thermal conductivity of the metal any bearing on the question or is the melting point partly responsible? I have had an idea that the built-up edge represents material of the work that actually welds to the tool. It would seem that high polish that cuts down frictional resistance and high melting point of the tool might both be factors in its formation.

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* American Cutting Alloys, Inc.

† Watertown Arsenal.

P. M. McKenna.—Mr. Ernst, of the Cincinnati Milling Machine Co., has made a study of that and has shown some diagrams of the flow of chips under compression as in a tool material. He used soft metals to show how the chips flowed, and it seems from his reports that at higher speed there are mechanical—purely mechanical—reasons why there is not so much built-up edge that has to go over the end of the tool.

Member.—One of the most interesting things in this paper is the extremely simple apparatus for determining thermal conductivity. I do not suppose that it is absolute, by any means, but it is certainly simple. It is so simple that it is probably easier to determine the thermal conductivity than the electrical conductivity, and assume there was a relation.

Has any one any information on the relation between the thermal and the electrical conductivity for these carbides at room temperatures, and also at higher temperatures?

P. M. McKenna.—We have made one or two tests for electrical conductivity, and applying a factor we found in the physics textbooks, or the critical tables, of the Wiederman-Franz ratio, we obtained an approximation to the correct result for electrical conductivity versus thermal conductivity. Unfortunately, only one or two specimens were observed in that way.

As to the method of determination, I have been warned by some physicists that this apparatus is too simple. But we used very pure lead and Armco iron, and a number of materials, finding that they gave the results reported in the critical tables within one part in eighty, and for our purposes it seemed to be very helpful, especially as we found the constituents of the same tools could be traced in their changes during heat-treatment by changes in the thermal conductivities.

F. M. Walters, Jr.,* Youngstown, Ohio.—In the discussion this morning it was remarked that these products of powder metallurgy were on a very small scale, and also that perhaps the precision with which pieces could be made was not very high.

I have it on very good authority that there are being produced for the cold-rolling of strip steel working rolls of tungsten carbide 32 in. long by 3 or 4 in. in diameter, and because of the thinness of the strip, the dimensions of the rolls have to be held to 0.0001 inch.

S. L. Hoyt,† Milwaukee, Wis.—Mr. McKenna has some very interesting figures in his table in which he makes use of the square of the valence divided by the two-thirds power of the atomic volume. Are the figures given for the value of that expression anywhere near proportionally correct values for the hardness?

P. M. McKenna.—They are in the table in the correct rank. Sodium chloride seems to be the softest of these materials; silver chloride is a little harder; sodium fluoride and lead sulphide are harder; calcium oxide is harder. There is only one exception—vanadium carbide is listed there from data reported in the literature which I do not believe are correct. The reason that vanadium carbide is misplaced in that table is because its properties have not been correctly observed. If it should be subsequently found that vanadium carbide is not misplaced, it is because its density and lattice are not what are reported in the table.

We have had great difficulty in making any vanadium carbide corresponding to this, as we have many of these other substances, and I think that will account for any differences. Also, the melting points are in the same range as these materials.

I speak only of rank as in the Mohs hardness scale. The quantitative evaluation of hardness is something that I do not know anything about.

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* Research Engineer, Youngstown Sheet & Tube Co.

† Research Metallurgist, A. O. Smith Corporation.

S. L. HOYT.—At any rate these would guide you to a group of materials for this type of application.

Your expression means, as I interpret it, that the greater number of atoms or valence electrons there are, or the closer they come together, the harder the material is, and if one could introduce another atom without materially altering the volume, the hardness should increase correspondingly.

In that connection, there is a group of compounds with which very little work has been done, the suboxides of some of the heavy metals. The addition of the single oxygen atom in these particular compounds apparently does not alter the lattice of the parent metal very much.

I was wondering whether you had paid any attention to those particular compounds.

P. M. MCKENNA.—I am not familiar with them. However, this paper is restricted to materials crystallizing in the phase-centered lattice. Of course, if the introduction of another atom changes the lattice form, the hardness would be different, and of course the planes on which the material would slip would be different, as in a diamond, which does not slip at all.

The formula used is absolutely unwarranted except that it does give this useful rank. It has been produced by Ernest Frederick, as you know, and is useful in arranging the materials into a rank, and if you find any new material of which you know the lattice constants and its density, you can estimate whether it would be hard or not in advance. It saves us from working nitrides, for example, which I believe demonstrable here as unlikely to be as good as carbides.

The Yield Point in Metals

By M. Gensamer, Member A.I.M.E.

(New York Meeting, February, 1938)

In applied mechanics and in metallurgy the transition from elastic to inelastic action is a matter of considerable interest and importance. Often the first inelastic deformation is apparently quite homogeneous; that is, uniformly distributed throughout the specimen. Sometimes this deformation is heterogeneous; that is, localized; inelastic deformation proceeds to some definite amount in restricted regions before adjacent regions of the specimen are inelastically deformed. In such cases the deformation does not become homogeneous until the whole specimen has been deformed the amount corresponding to that for each localized deformation. If the test is stopped before uniform extension sets in, the heterogeneous character of the deformation is apparent on the surface of the specimen through characteristic markings, which have been called "Lüders'" lines, "Hartmann's" lines, the "Piobert effect," or simply "flow figures." These markings are the source of considerable trouble in fabricating operations, particularly in the deep drawing of steel sheet. In many cases where the transition is of this nature, the stress developed at the upper limit of the elastic range is greater than the stress during the period of heterogeneous deformation, giving rise to the familiar "drop of the beam" effect in testing. The amount of the yield-point elongation, as well as the value of the stress at the lower yield point (the value to which the stress drops when yielding begins), are functions of the temperature and the testing speed. Lower temperatures and faster rates of testing increase both the yield-point elongation and the yield-point stress.

These matters have been ably discussed in a recent paper by Winlock and Leiter[1] though, as brought out by the discussion of that paper, the phenomena are but little understood. The purpose of the present paper is to clarify the problem through the application of a simple principle, and to show that, through the application of this principle, a number of phenomena in the plastic deformation of metals become more readily understood.

The principle is this: During homogeneous flow, the rate of work-hardening is greater than the rate of change of stress resulting from change

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Manuscript received at the office of the Institute Dec. 1, 1937.

* Assistant Professor of Metallurgy and Member of the Staff of the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

[1] References are at the end of the paper.

of area; during heterogeneous flow, the relative magnitudes of these two rates are reversed. The instant of transition between homogeneous and heterogeneous flow is characterized by equality in these rates. This principle was developed several years ago by Dr. Anson Hayes and has been stated recently.[2,3] The phrase "rate of work-hardening" means simply the slope of the stress-strain curve.

Consider the tensile test. During the period of homogeneous flow, the resistance to flow caused by work-hardening is increasing at a greater rate than the tensile stress is increasing as a result of the diminution of area, and it is necessary in order to maintain flow to increase the applied load continuously; during this period, local flow can proceed to only a slight extent because the part that flows work-hardens and the flow is transferred to a neighboring region. After the transition, that is, after necking-down has begun, the specimen elongates locally (heterogeneous flow) because the rate of increase of tensile stress caused by diminution of area is greater than the rate of increase of resistance to flow caused by work-hardening; the difference between the resistance to flow and the applied stress is greater in the region already flowing than in the neighboring regions, and flow proceeds at an accelerating rate in the necking-down part. As a result of this action it is well known that in the usual testing machine the applied load reaches a maximum at the instant necking-down begins. In dead-weight testing, the same argument applies to the transition from homogeneous to heterogeneous flow, although in this case, of course, the load is constant throughout the test.

It is also well known that in the ordinary tension test of a sample of annealed mild steel, the transition from heterogeneous to homogeneous flow, which marks the end of the period of flow by the formation of Lüders' lines, is characterized by a minimum in the applied load curve. In both ordinary and dead-weight testing, this transition is also characterized by equality of the rates of increase of stress caused by reduction of area and of resistance to flow caused by work-hardening.

Since, then, these transitions in both directions—that is, from heterogeneous to homogeneous and from homogeneous to heterogeneous flow—are the result of equality in the rates of increase in stress brought about by diminution of area and by work-hardening, it should be profitable to analyze these processes.

Let the extension ε be defined[4] by the relation

$$\varepsilon = \int_{l_0}^{l} \frac{dl}{l} = \ln \frac{l}{l_0} \qquad [1]$$

so that

$$l = l_0 e^{\varepsilon} \qquad [2]$$

where ε is the extension, l_0 is the original gauge length, l is the instantaneous gauge length, and e is the base of the natural system of logarithms. Through the constancy of volume relation,

$$V = Al = A_0 l_0 \tag{3}$$

$$A = \frac{A_0 l_0}{l} = A_0 e^{-\varepsilon} \tag{4}$$

where A is the instantaneous cross-section area, and A_0 is the original cross-section area. If P is the load applied to the specimen, then

$$P = \sigma A \tag{5}$$

where σ is the tensile stress. Then

$$P = \sigma A_0 e^{-\varepsilon} \tag{6}$$

so that

$$\frac{dP}{d\varepsilon} = A_0 e^{-\varepsilon}\left(\frac{d\sigma}{d\varepsilon} - \sigma\right) \tag{7}$$

from which, since $\dfrac{dP}{d\varepsilon} = 0$ at a maximum or a minimum in the load vs. strain or P/A_0 vs. strain curves, we obtain

$$\left(\frac{d\sigma}{d\varepsilon}\right)_P = \sigma \tag{8}$$

This is the rate at which the stress is increasing as a result of the extension of the specimen and the accompanying decrease in area, and it is also the slope of the flow curve at the instant of transition from heterogeneous to homogeneous or from homogeneous to heterogeneous flow.

The rate at which the resistance to flow is increasing or decreasing as a result of work-hardening may be taken from a Ludwik flow curve* using only the part of the curve that applies to the periods of homogeneous flow, for it is only during homogeneous flow that the true strain is known. The curve may be extended into the heterogeneous-flow regions by extrapolation. Ludwik has shown that many of these curves are expressed by equations of the form

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* In this country commonly called a true stress-strain curve; see C. W. MacGregor.[5] Ludwik's flow curve is correctly the shear stress calculated from the applied load and the least area of the specimen, plotted against the specific shear strain, calculation of which from the extension depends on the number of active shearing planes. Thus Ludwik obtains for dihedral shear $\gamma = 2\varepsilon$, while for octahedral shear Nadai[6] obtains $\gamma = \sqrt{2} \cdot \varepsilon$. In this connection it should be pointed out that the straight-line part of what is known as a true stress vs. effective deformation curve is the result of the increase of the ratio of normal to shearing stress, arising from the change in shape of the specimen after the beginning of necking; it does not represent the actual normal stresses, which vary from point to point, nor does it give the true shearing stresses on which a study of plastic behavior in forming operations should be based. The true flow curve should assymptotically approach a maximum value of the stress, which represents the limit of work-hardening capacity for the metal. This limit will seldom be realized in the tension test, for fracture (propagation of a crack) interrupts the process, and the specimen breaks at what Kuntze has called the technical cohesive strength.

$$\sigma = \sigma_0 + k\sqrt[n]{\varepsilon} \qquad [9]$$

which may be plotted as

$$\log(\sigma - \sigma_0) = \log k + \frac{1}{n}\log\varepsilon \qquad [10]$$

and so extrapolated as a straight line. Since there is no reason to believe flow curves to be discontinuous, it should always be possible to make a reasonable extrapolation, even though equations 9 and 10 may not apply.

Knowing these rates of increase in stress, it is possible to predict not only the limit of uniform elongation in any particular flow process, which has already been done by Nielsen[7] for necking-down in the tension test, but also the limit of heterogeneous action at the transition from flow at the yield point with the formation of Lüders' lines to homogeneous flow. Further, it is possible to predict the effect of varying the rate of testing on the amount of elongation at the yield point, which has been studied experimentally by Siebel and Pomp[8] and more recently by Winlock and Leiter.[1]

If the flow curve can be expressed by an equation, the extension at the yield point and at necking-down can be calculated by finding the points on the curve at which $\frac{d\sigma}{d\varepsilon} = \sigma$, where $\frac{d\sigma}{d\varepsilon}$ is the slope of the flow curve and σ is the stress. (It can be shown that this is the same as $\frac{d\sigma}{d\lambda} = \frac{\sigma}{1 + \lambda}$ where $\lambda = \frac{l - l_0}{l_0}$, for a σ vs. λ curve; this is the condition used by Nielsen to predict the point of necking.) If, for instance, $\sigma = \sigma_0 + k\sqrt[n]{\varepsilon}$ (Ludwik's equation),

$$\frac{d\sigma}{d\varepsilon} = \frac{k}{n}\varepsilon^{\left(\frac{1}{n}-1\right)} \qquad \text{and also} \qquad \frac{d\sigma}{d\varepsilon} = \sigma = \sigma_0 + k\sqrt[n]{\varepsilon}$$

or

$$k\varepsilon^{\frac{1}{n}} - \frac{k}{n}\varepsilon^{\left(\frac{1}{n}-1\right)} + \sigma_0 = 0 \qquad [11]$$

If the value of $\frac{1}{n}$ is such that this equation can be solved analytically, the values of ε so obtained will be the limits of uniform extension.

A graphical solution is much simpler. An easy graphical solution is obtained by matching the flow curve (true stress σ vs. extension ε) against a curve which gives, for every point on the flow curve, the rate at which the stress is increasing as a result of the diminution of area. This curve is obtained by integration of equation 8, or more simply from the relation

$$P = A_1\sigma_1 = A_2\sigma_2$$

from which is obtained

$$\sigma_2 = \sigma_1 \frac{A_1}{A_2} = \sigma_1 \frac{A_0 e^{-\varepsilon_1}}{A_0 e^{-\varepsilon_2}} = \sigma_1 e^{(\varepsilon_2 - \varepsilon_1)} \qquad [12]$$

To plot this, we may take $\sigma_1 = 1$ and $\varepsilon_1 = 0$, so that the curve that is to be matched to the flow curve is given by

$$\sigma = e^{\varepsilon} \qquad [13]$$

Hereinafter, this curve will be called the control curve. The matching is accomplished by moving the control curve parallel to the ε axis until the two curves intersect or are tangent, in this way choosing the appropriate value of σ_1 and ε_1. Where the slope of the control curve is greater at the intersection than the slope of the flow curve, the deformation will be heterogeneous; where the slope of the control curve is less than the slope of the flow curve, the deformation will be homogeneous; and the points of tangency found in this way will be points of transition between periods of homogeneous and heterogeneous flow.*

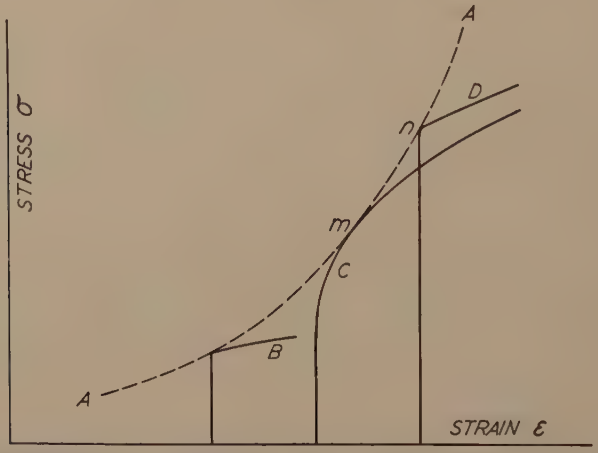

FIG. 1.—JUXTAPOSITION OF CONTROL CURVE AND FLOW CURVES. TRANSITION FROM HOMOGENEOUS TO HETEROGENEOUS FLOW OCCURS AT POINT OF TANGENCY.

Fig. 1 illustrates the application of the method to three types of flow curves,† considering only the point of necking-down, or maximum load corresponding to the tensile strength. The curved line A-A is part of the curve $\sigma = e^{\varepsilon}$ (the control curve), which can be moved horizontally to intersect or be tangent to the flow curves at various points; it represents the rate of increase of stress resulting from diminution of area during flow in tension. For curve B, which represents a material with a low yield point and a low rate of work-hardening $\frac{d\sigma}{d\varepsilon}$ throughout its extension, the slope of the plastic part of the curve is always less than that of the control curve, so that the rate of work-hardening is always less than the rate of increase of stress due to diminution of area, and flow will be heterogeneous; that is, the specimen will begin to neck-down immediately and proceed to fracture with no period of homogeneous flow. If, after reaching the yield point, the load is maintained constant, as in a dead-weight test, the curve A-A represents the stress throughout the test, and since the rate of flow increases with the difference between the applied stress and the resistance to flow at equilibrium, or the instantaneous yield point from curve B, the rate of flow will continue to increase until fracture. Fracture will occur when the applied stress reaches the technical cohesive strength, given by the intersection of curve A-A with the Kuntze technical cohesive strength curve.[9] In brittle materials this point may be reached with fairly low values of extension, and so little deformation will occur, and all of it will be local; these are the shearing types of brittle fractures. This is also the type of fracture that occurs at the rim of the cup in the tensile test of a ductile metal.

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* The same thing could, of course, be done by Nielsen's method for σ vs. λ curves $\left(\text{where } \lambda = \frac{l - l_0}{l_0}\right)$ by drawing lines tangent to the curve and through the point $\sigma = 0$, $\lambda = -1$. The use of σ vs. ε curves, as in this paper, offers some theoretical advantages.

† In plotting these curves, ε is calculated from the relation $\varepsilon = \ln \frac{l}{l_0} = \ln \frac{A_0}{A} = 2 \ln \frac{d_0}{d}$.

For tests carried out in a rigid testing machine, the stress will be maintained on the curve B (which is drawn for a particular rate of straining); because a small extension results in a lowering of the applied load P and hence σ, and no flow will occur until the stress is again raised to the curve B. In this case the control curve does not give the actual rate of increase in stress, for the load P is not constant; however, this change in load P applies to both the deformed and undeformed regions and for this reason does not affect the validity of our criterion for transition, so that homogeneous flow cannot occur after yielding for curve B.

If the rate of work-hardening is greater, as for curve C, homogeneous flow will occur up to point m at which point the slope $\frac{d\sigma}{d\varepsilon}$ is equal to σ, as shown by tangency to the control curve. By moving the control curve horizontally, it may be seen that below m the rate of work-hardening is greater than the rate of increase of applied stress due to flow, and flow is homogeneous; above m the reverse is true, and flow proceeds by necking-down and continues until the actual stress reaches the Kuntze curve. In a dead-weight test, flow will not proceed to fracture until a load is applied that will produce a stress greater than σ_m at the point m; beyond this point the stress will increase at constant load along the curve A-A to fracture. The load that will just cause fracture is given by $A_m\sigma_m$. The stress $\sigma_0 = \frac{A_m\sigma_m}{A_0} = \sigma_m e^{-\varepsilon_m}$ may be taken as the creep strength, for at any load below $A_m\sigma_m$ flow will proceed as along the curve A-A (displaced horizontally so as to pass through the initial stress) to its intersection with the flow curve C, and then stop. Loads greater than $A_m\sigma_m$ will produce the flow described by the familiar three-stage creep curve (λ vs. time), for the rate of flow will increase with the difference in stress between the flow curve C and the actual stress given by the displaced A-A curve. This assumes, of course, that the flow curve is not altered during the test, as it actually is in practice.

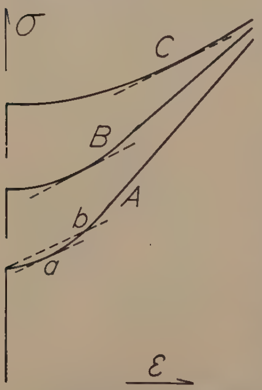

FIG. 2.—FLOW CURVES REQUIRED FOR HETEROGENEOUS FLOW (LÜDERS' LINES) AT YIELD POINT IN TENSION.

Increasing speed of test (A is slow, C is fast) increases yield-point elongation, determined by point of tangency to control curve.

Curve D may be used to explain the lowering of the amount of uniform elongation by any treatment that will raise the yield point and lower the rate of work-hardening. This can be accomplished by cold-work, hardening heat-treatments, lowering the temperature of test, or raising the speed of testing. The material of curve C will begin to neck at m; the hardened material, yielding curve D, will neck at n.

Now consider the yield point. If flow curves were all like those illustrated in Fig. 1, the phenomenon of heterogeneous flow at the yield point would never be observed. What is required for such yielding (giving rise to flow figures) is a flow curve like those shown schematically in Fig. 2. The continuous lines are flow curves; the dashed lines are parts of the control curve. The material will flow heterogeneously to the point of tangency of the flow curve and the control curve, as at a on curve A, Fig. 2. Such flow curves could be obtained experimentally, of course, only by the use of the most rigid testing machine, so that a slight amount of flow would permit the applied stress to fall below the flow curve; otherwise the material will continue to flow to the intersection of the actual stress curve and the flow curve, a point that is beyond the limit of heterogeneous flow (for example, point b on curve A for deadweight testing, or some point between a and b for the usual testing machine). In any case, the curve below a can only be drawn by measuring the extension within a flow band.

A fair amount of indirect evidence supports the view that such curves are typical, even in nonferrous metals. Yield points have been observed in copper[10] and even in single crystals of gold-silver solid solutions.[11] (Copper exhibits well developed upper and lower yield points at −30° C.)

Scrupulously careful work is necessary to obtain a yield point when the stress at the yield point is low, as should now be obvious from a consideration of curve *A-A*, Fig. 1. The slope of the control curve is so low at low values of applied stress that the amount of extension at the yield point must be extremely small, and possibly absent entirely if the metal begins to work-harden immediately. For high yield points a yield-point elongation may be easy to detect, for the point of tangency demarking the limit of heterogeneous flow will occur at greater values of ε the higher the stress at the yield point and the less the rate of work-hardening. Any system of internal stresses or departure from uniformity in the applied stresses will make it quite impossible to detect a yield point where the yield point elongation is small. The author has found yield points in single crystals of iron (the yield point in iron single crystals had previously escaped detection) by careful stress-relief annealing and a very careful step-wise loading. In polycrystalline metals such uniformity in stress may be impossible of achievement, and this, coupled with the greater rate of work-hardening, may make the detection of a yield point impossible. The induction-period phenomenon in creep (reported in discussion of Winlock and Leiter's paper by the author) requires and is completely explained by flow curves like those in Fig. 2.

The important conclusion to be drawn from these considerations is that two metals, one of which in the tensile test exhibits an elongation at the yield point and develops Lüders' lines and the other of which does not, *need* differ only in degree and not in kind. The flow curves may be similar in character, but through differences in the value of the stress at the yield point and the rate of work-hardening these quite dissimilar behaviors on yielding result.

The transition from curve *A* to curve *C* in Fig. 2 may be brought about by increased speed of testing, among other factors,* and this provides an explanation for the results of Siebel and Pomp and of Winlock and Leiter on the effect of testing speed on the yield point of mild steel. The general shape of these curves and the effect of speed, temperature, and alloying on them, are easily reconciled with modern notions on work-hardening and recovery.[13]

Flow figures beyond the yield point, as in some aluminum alloys and 18-8 stainless steel, must be the result of fluctuations in the rate of work-hardening. Such fluctuations are probably brought about by strain-aging during the test.

Although the curves of Fig. 2 are adequate to account for heterogeneous flow and an extension at the yield point in tension testing, they are not typical of true stress-strain curves for mild steel, for they fail to provide an explanation for flow figures in compression, and for the *upper* yield point in both tension and compression. For these it must be admitted that the flow curve drops after flow begins, as is illustrated in Fig. 3; for in compression flow diminishes the applied stress, and the control curve has a negative slope, so that the flow curve can be tangent to the control curve only if the resistance to flow (work-hardening) is diminishing. (In compression there can be, of course, no necking-down phenomenon, for beyond the yield point the slope of the control curve remains negative and that of the flow curve is always positive, yielding homogeneous deformation.) Such curves can be explained on the basis of grain-boundary resistance, which must be broken down before flow can begin; once flow begins, stress concentration at the junction of the deformed and undeformed regions keeps the stress locally above the upper yield-point value and reduces the necessary value of the average stress. In this connection the term "grain boundary" is used loosely; any discontinuity in structure (perhaps even G. I. Taylor's semi-opaque crystal imperfection boundaries!) may be so regarded. On this basis may be explained the high value of the upper yield point when tension tests are carefully carried out in rigid machines.

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* D. W. Ginns[12] has made the most recent demonstration that high speed in testing raises the yield point but has little effect on the tensile strength, hence diminishes the rate of work-hardening.

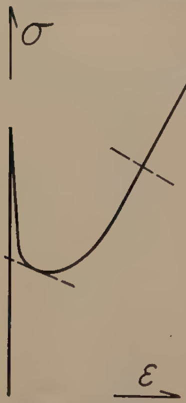

FIG. 3.—FLOW CURVE REQUIRED FOR HETEROGENEOUS FLOW AT YIELD POINT IN COMPRESSION. SLOPE OF CONTROL CURVE IS ALWAYS NEGATIVE.

If the ideas presented above are sound, it will be admitted that the rate of work-hardening is an important property, in fact discriminative, and worthy of detailed investigation. Physicists and metallurgists who have considered work-hardening are generally agreed that its cause lies in the development of imperfections in the crystal lattice, such as fragmentation, rotation of fragments, or crystal-plane rumpling.[14] These phenomena, while undoubtedly contributing to some extent to hardening, ought to be irreversible, and are quite inadequate to explain the Bauschinger effect. A more satisfactory explanation is one based on the development of internal stresses.[15,16] The author likes to believe that metals have an elastic limit that is inherently higher than that developed by a polycrystalline aggregate, and which is strongly dependent on grain size; but that stress concentrations produce local yielding before the average stress reaches this value; and that on release of the external load, the parts that have suffered deformation are put into compression (if the specimen was first strained in tension). This results in an increased elastic limit in tension and a lowered elastic limit in compression. Such an explanation for work-hardening provides a simple cause for the process known as elastic recovery,[13] by which the yield point of a cold-worked metal becomes gradually lower, without recrystallization, approaching the value of the metal before cold-working; the speed of this process is strongly dependent on the temperature, and it is frequently obscured by strain-aging. If work-hardening is the result of internal stresses (arising from nonuniform deformation), recovery is simply creep or flow under the action of these internal stresses; as creep proceeds the stresses are lowered and the yield point recedes toward the original value.

As to the cause of the *increasing* slope of the flow curve after flow has just begun (as in curve A of Fig. 2), it is likely that this is produced by strain-aging superimposed on the normal curve, for the normal curve might reasonably be expected to exhibit a decreasing slope as extension proceeds (as in curve C of Fig. 1) rather than an increasing one. Indeed, it has frequently been suggested that the phenomenon of heterogeneous flow at the yield point, and the associated upper and lower yield points, are characteristics of a strain-aging material and are not to be found in materials free from strain-aging (ref. 4, p. 53). Increasing the speed of testing, by delaying the strain-aging effect, should increase the amount of elongation at the yield point, for then the point of tangency of the flow curve and the control curve will be displaced to greater values of the extension; while increasing the temperature, by accelerating aging, should diminish the yield-point extension.

Finally, it is necessary to consider the relation of the above to the most important work which has been done in this field, that of A. Nadai and his coworkers.[17,18] Dr. Nadai has not only developed a masterly treatment of the problem of the location of flow figures under various stress conditions, and shown the engineering importance of flow figures as guides to the distribution of stress in complicated cases, but he has originated the prevailing theory of the cause of the drop in stress when flow begins (the upper and lower yield point effect). Briefly, Dr. Nadai postulates a grain-boundary network of strong material which increases the ability of the metal to sustain an elastic stress. He has shown that flow figures are produced, even in metals that ordinarily do not exhibit them, by holes or grooves which concentrate the stress or weaken the material, and so suggests that flow figures in steel are the result of the development of local weakness coincident with the elastic failure of the metal. This leads to the drop of the load on yielding. If the author of the present paper has made any contribution beyond that of Dr. Nadai, it lies in clarifying the problem of the ending of local flow and the beginning of homogeneous flow, and in offering a treatment that may be capable of explaining the observed effects of speed of testing and temperature on the location of this transition.

The author wishes to acknowledge that comments from Dr. Nadai have caused him to make several changes in his paper, particularly in the form of equation 12, for which he is very grateful; and to acknowledge the stimulating discussion over a long period of time with members of the staff of the Metals Research Laboratory and the graduate students of the Carnegie Institute of Technology.

SUMMARY

The more important of the points developed are:

1. A transition between homogeneous and heterogeneous flow will occur at every point on a flow curve (true stress σ vs. strain ε) when the slope equals σ.

2. Whether or not the yield point will be characterized by heterogeneous flow (Lüders' lines, the Piobert effect) is determined by the value of the stress at the yield point and the rate of work-hardening of the material; the lower the stress at the yield point and the greater the rate of work-hardening, the less will be the yield-point elongation and the more difficult its detection. If the slope of the flow curve is initially greater than σ, flow at the yield point will be homogeneous.

3. Increasing the speed of the test raises the yield-point stress and lowers the rate of work-hardening, and consequently increases the amount of elongation at the yield point. This is explained by considering the effect on the stress-strain curve to be expected of strain-aging. The effect of changing the testing temperature may be similarly explained.

4. It is necessary to pay more attention to the theory that work-hardening is caused by the development of internal stresses; this theory provides a simple explanation for elastic recovery.

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DISCUSSION

(L. W. McKeehan presiding)

R. W. E. LEITER[*] AND J. WINLOCK,[†] Philadelphia, Pa. (written discussion).—Dr. Gensamer is to be congratulated for his clear presentation of the principles of deformation as applied to the changes occurring at the maximum load in any tensile test. We cannot agree, however, with Dr. Gensamer in regard to the application of these ideas to the phenomena taking place at the yield point of unstrained low-carbon steel. Our most recent published ideas on "Lüders" line phenomena appear in our discussion of R. F. Miller's and W. E. Milligan's paper.[‡]

H. F. MOORE,[§] Urbana, Ill.—It seems to me, as a testing engineer, that the phenomena Dr. Gensamer describes and the explanation of them which he gives fit with what we observe in practice. I believe that he has given a picture of inelastic action that is worth careful examination by every testing engineer, and that may possibly suggest new indices for elastic strength. Dr. Gensamer's picture looks complicated now, but extremely complicated methods can frequently be reduced to ease of application by graphic or other means.

As a member of the A.S.T.M. Committee E-1 on Methods of Testing, I intend to request that every member of the Section on Elastic Strength be furnished with a copy of this paper and that they read it thoroughly.

F. G. TATNALL,[||] Philadelphia, Pa.—It has been said that the upper and lower yield points are two distinct phenomena. The upper yield point is said to be unstable but the lower yield point is considered an important property. I have been trying to find out all about the lower yield point, since it seems to be the governing element in this picture and will determine the susceptibility of sheet material to development of stretcher strains. Winlock and Leiter have asked why aluminum and copper do not show the peculiar yield effect of mild steel. In conversation, Dr. Gensamer said yesterday that aluminum and copper do show the upper and lower yield-point effect. The cause of the difference between the smooth curve versus the sharp drop at the yield point is something that very few people understand, and as a builder of testing machines we are anxious that it be thoroughly understood.

L. W. MCKEEHAN,[¶] New Haven, Conn.—How could the control curve get a negative slope? It is bound to occur in compression, because the relative magnitudes of σ_2 and σ_1 change, so that the exponent has to be negative. But I do not see how the slope can become negative in tension.

M. GENSAMER.—Answering Professor McKeehan, the slope never does become negative in tension. If the slope of the flow curve is negative, the deformation is heterogeneous, and it cannot be homogeneous until the slope of the flow curve becomes greater than the slope of the control curve, which is always positive in tension.

As to Mr. Tatnall's point, Fig. 4 shows a curve for Armco iron that resembles flow curves obtained for some aluminum alloys. This is for Armco iron. The first curve on the left is for annealed Armco iron. You will note that we do not have what I have been calling a yield point until considerable deformation has occurred; that is, the yield point that I have been discussing does not coincide with the proportional limit. The material has a yield strength at a lower value of stress than the yield point. This material was carefully annealed. The specimen was very carefully prepared. The loading was as axial as I know how to make it. I have tested for axiality of loading by using four extensometers placed around the specimen. I know the stress is uniform to within at least one per cent, and so this departure from a straight-line relationship below the yield point is not to be explained by departure from axiality of loading. Note that on reloading after some plastic deformation, we get a straight line right up to the yield point. The continuation of the first curve shows that effect.

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[*] Research Metallurgist, Edward G. Budd Mfg. Co.

[†] Chief Metallurgist, Edward G. Budd Mfg. Co.

[‡] R. W. E. Leiter and J. Winlock: Discussion on Influence of Temperature on Elastic Limit of Single Crystals of Aluminum, Silver and Zinc. *Trans.* A.I.M.E. (1937) **124,** 248.

[§] Research Professor of Engineering Materials, University of Illinois.

[||] Baldwin-Southwark Co.

[¶] Director, Sloane Physics Laboratory, Yale University.

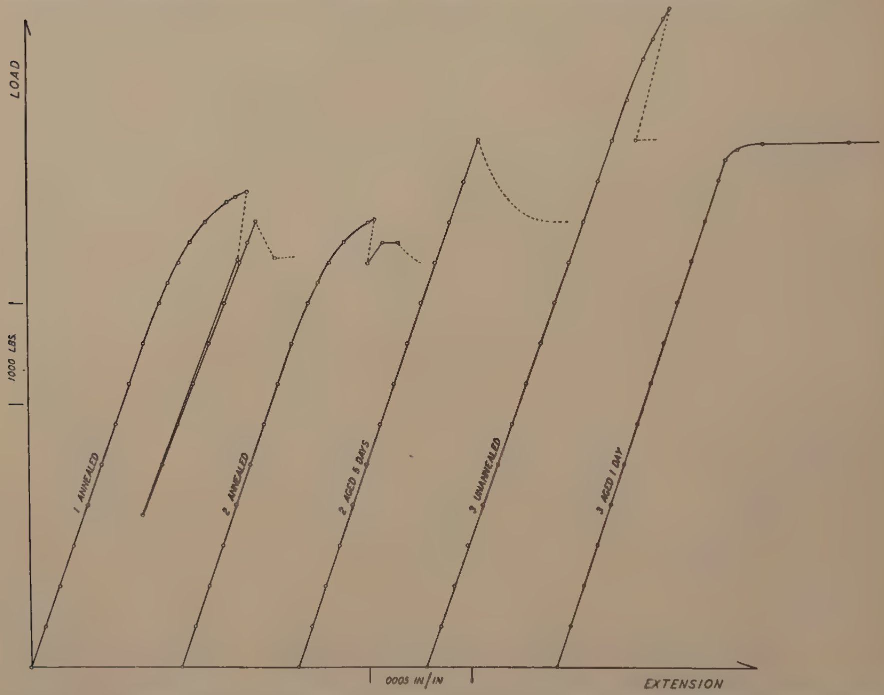

FIG. 4.—STRESS-STRAIN CURVES FOR ARMCO IRON, SLOWLY COOLED AFTER ANNEALING BELOW THE CRITICAL TEMPERATURE AND AGED AFTER STRAINING.

The second curve (marked 2 annealed) is just another check test on the first one. The third curve (marked 2 aged 5 days) is for the No. 2 sample after aging for five days at room temperature. There Hooke's law is obeyed within the sensitivity of the extensometer (which is roughly 10^{-6}), right up to the yield point.

This is the behavior we ordinarily observe in carefully prepared specimens of mild steel, and I am now of the opinion that it is so because all of these mild steel specimens have been strain-aged. The Armco iron of these tests was annealed below the critical and cooled slowly after machining, and so was not strain-aged before the test. I expect that in a good many cases where we have strain-aging we can have yield points. Fig. 5 shows a curve for duralumin which has a bump in the stress-strain curve at the left after aging. If that were a little more pronounced, we could expect a yield point with heterogeneous deformation on yielding, and frequently for some alloys of aluminum we get flow figures showing up on the specimen some time after extension has been going on homogeneously, probably because of strain-aging during the test.

(Written discussion). I want to thank Professor Moore for his comments, and to say that I do not believe what I have written will cause any furor in his committee E-1. All that I am seeking here is a clear view of what is going on at the yield point, so that we, as metallurgists, may explain the yield-point phenomena.

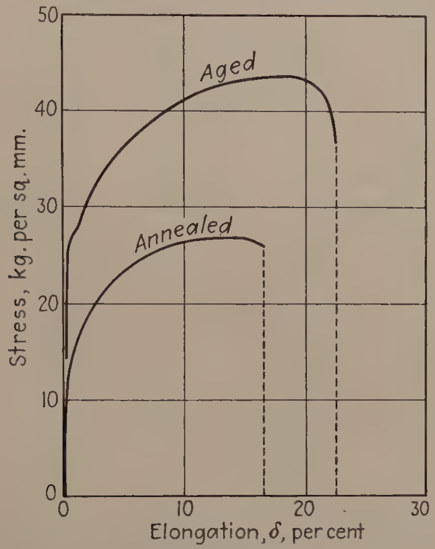

FIG. 5.—STRESS-STRAIN CURVES FOR AGED (ABOVE) AND ANNEALED (BELOW) DURALUMIN.

From W. Kuntze: *Ztsch. Metallkunde* (May, 1934) [5] **6,** 106–112.

I had expected a longer discussion from Messrs. Winlock and Leiter, for I have had a long talk about this matter with Mr. Winlock and know his views, and how they differ from mine; and also, how close we are to an agreement. Mr. Winlock is earnestly seeking a *cause* of the lowered resistance to deformation once deformation has begun, and in this paper I pay little attention to cause. I hope to establish the cause and am working on it, but I must confess with discouraging results. What I hope to have demonstrated is that a yield-point elongation with drop in load is a necessary consequence of a low rate of strain-hardening, and that the factor that requires a metallurgical explanation is this low rate of strain-hardening. I cannot agree that a set of conditions that produce heterogeneous flow at one stage in the flow process should not have the same effect at another stage.

Creep and Fracture Tests on Single Crystals of Lead

By John B. Baker,* Bernard B. Betty,† and H. F. Moore‡

(New York Meeting, February, 1938)

For several years there has been in progress in the Materials Testing Laboratory of the University of Illinois an investigation of creep and fracture of lead and lead alloys. In the course of this investigation it has been shown that the phenomenon of creep occurs in part at the grain boundaries of lead and lead alloys. To study the occurrence of creep and the development of fracture within crystalline grains, two series of tests of single crystals of lead have been carried out. The first of these, a preliminary series, by Mr. Betty, has been described.[1,2] The second, pursued by Mr. Baker for his doctoral dissertation, was carried out under the direction of Professor Moore, with the assistance of Prof. G. L. Clark in the X-ray work, and the cooperation and advice of Mr. Betty. This paper is based on the test data obtained in this second series.

Single crystals of a very pure commercial lead have been prepared, some of them tested to measure creep, others tested to fracture under long-continued steady load, and still others tested under cycles of repeated tension. An interpretation of the test data of these single-crystal tests is offered, which is a combination of parts of several well-known theories.

SPECIMENS

The single-crystal specimens were made from a piece of very pure commercial lead sheathing. A spectroscopic analysis of one of the single crystals showed the presence of 0.005 per cent Bi, 0.0001 per cent Cu and 0.0003 per cent Ag.

Preparation.—The Bridgman method of casting single-crystal specimens was used.[3] The specimens were cast to the shape and size shown in Fig. 1 (dimensions in Fig. 4*c*) in a duralumin mold. Molten lead does not stick to duralumin. Fig. 1 shows the mold and the blast flames for heating. After the mold had been heated to the temperature of molten

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Manuscript received at the office of the Institute Nov. 22, 1937.

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[1] References are at the end of the paper.

lead it was filled with molten metal. Then the mold was heated further to eliminate nuclei that might act as centers of crystallization on cooling. Next a temperature gradient was established along the mold by making the flames impinge upon its top, and by raising a vessel of water to the position shown in Fig. 1. The blast flames were then turned down gradually, and the molten metal cooled in the form of a single crystal—if the process was successful. Usually there was obtained one single-crystal specimen for every four or five attempts.

The surface of the new casting was rather sensitive to an etchant composed of 4 parts nitric acid (sp. gr. 1.72), 3 parts glacial acetic acid and 16 parts water.[4] Different crystals have different directional reflecting power for light, and the presence of a second crystal in the specimen could be detected readily. Thirty-four single crystals were thus prepared.

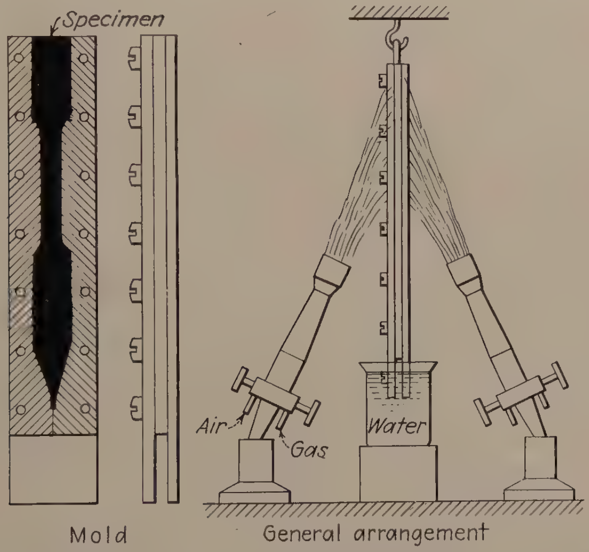

FIG. 1.—MOLD AND APPARATUS FOR MAKING SINGLE-CRYSTAL SPECIMENS OF LEAD.

The specimens were heated slowly to 540° F. and held at that temperature for about 100 hr., after which they were cooled slowly for a period of about 100 hr. After cleaning in the etching reagent, the specimens were successively washed in water, alcohol and ether. The ether was removed from the specimens by means of an air blast. Specimens thus prepared retained their silvery luster for a considerable period of time.

Space-lattice Orientation.—The orientation of the face-centered cubic space-lattice cells, which make up a single crystal specimen of lead, was determined by the method of light reflection as described by Bridgman,[3] some details of his method being slightly modified. As shown in Fig. 2, a single-crystal specimen was placed with its axis along the diameter of a transparent celluloid sphere. This sphere, with the specimen inside, was taken into a room with a single ceiling light and held directly under the light and rotated until a flash of light, constituting a regular reflection from the myriads of tiny facets on the surface of the crystal, was observed. While the sphere and specimen were being held in this position, the position on the surface of the sphere at which the image of the overhead light was mirrored was marked with washable ink. This point on the sphere was the point of tangency of a plane that was parallel to the tiny facets reflecting the light from the surface of the sphere. By further rotating and spotting points on the sphere, it was found that eight reflection spots were observed. These eight reflection spots (four pairs) correspond to the four pairs of octahedral planes, planes of maximum atomic density, maximum distance from the nearest parallel atomic plane, maximum reflecting power, and the only planes on which slip has been observed to occur.[5,6,7] Using an equatorial and a polar plane of the sphere as reference planes, the polar coordinates of the reflection spots on the sphere were measured. Then it was possible to write the equations of the tangent planes in terms of three rectangular coordinates, one along the axis of the specimen, a second perpendicular to the width of the specimen, and the third perpendicular to the thickness of the specimen. The eight octahedral planes constitute four pairs of parallel planes, so that, knowing the equations for four planes, it is a matter of trigonometric computation to determine the orientation of the space-lattice cells with respect to the axis of the specimen.

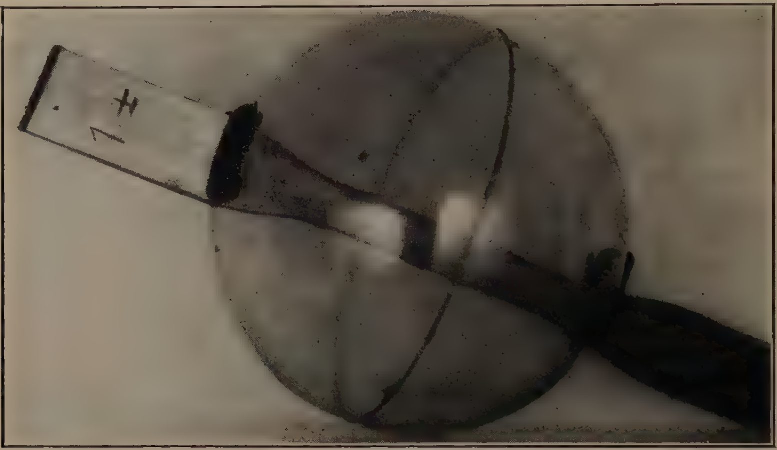

FIG. 2.—CELLULOID SPHERE AND SPECIMEN FOR DETERMINING ORIENTATION BY BRIDGMAN REFLECTION METHOD.

RESOLVED SHEAR STRESS

Data have been presented[5,6,7] which indicate that in face-centered cubic metals slip occurs between parallel atomic planes whose interplanar distance is a maximum. The planes of greatest atomic density are such planes. Furthermore, the data indicate that any slip that may occur will take place in the direction of greatest linear atomic density on one or more of those planes. In the lead crystal, considering only one of each pair of parallel octahedral planes, the plane of maximum atomic density is any one of four octahedral planes, and the line of greatest density on an octahedral plane is any one of its three intersections with the other octahedral planes. There are twelve of these directions of potential slip, three on each of four octahedral planes.

The component of shear stress developed along any of these slip directions can be computed, and such a component is called a "resolved shear stress." For the computation of all the resolved shear stresses only the space-lattice orientation, the dimensions of the specimen and the applied load are needed. If the (111) plane is designated by 1, the $(1\bar{1}1)$ plane by 2, the $(\bar{1}\bar{1}1)$ plane by 3, and the $(\bar{1}11)$ plane by 4, the resolved shear stress along the intersection of, say, (111) and $(\bar{1}\bar{1}1)$ may be designated by the symbol S_{13}.

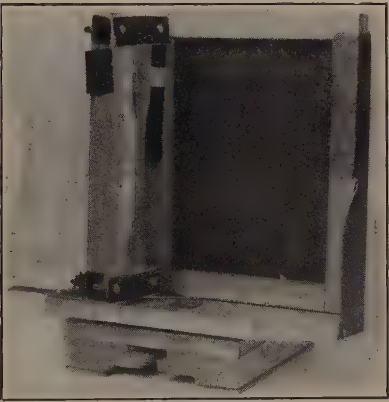

FIG. 3.—CASETTE FOR HOLDING SPECIMEN BEING EXPOSED TO X-RAYS.

X-RAY EXAMINATION OF SINGLE-CRYSTAL SPECIMENS

X-ray patterns of the crystal structure were prepared by the Laue method, using heterogeneous ("white") radiation. Laue diagrams and white radiation were used because of availability of equipment, and the X-ray photograms have been interpreted in the light of that technique. The specimens being of lead, it was impracticable to use a transmission process, and the X-ray beam was reflected from the surface of the specimen at a small angle. The crystal structure of lead has a fourfold symmetry, and hence the Laue spots may be expected to fall upon four large ellipses, but the orientation of the specimens and the absorption of the lead were such that generally only one large ellipse appeared on the film. *K*-alpha radiation from a molybdenum-target Phillips Metallix tube, operating at 30,000 volts and 20 milliamperes, was used to obtain a pattern with a 4-hr. exposure.

The holders (casettes) for the specimens (Fig. 3) were so made that the angle of reflection could be measured or reproduced. The specimen could be moved parallel to the film at a constant film-to-specimen distance of 3 cm. The film was offset to permit the recording of spots at higher glancing angles.

The Laue interference spot should be a smooth-edged ellipse if the reflecting surface is a plane. The size of the spot is a function of the diameter or definition of the X-ray beam and the thickness of sample penetrated. If for any reason the reflecting surface does not remain

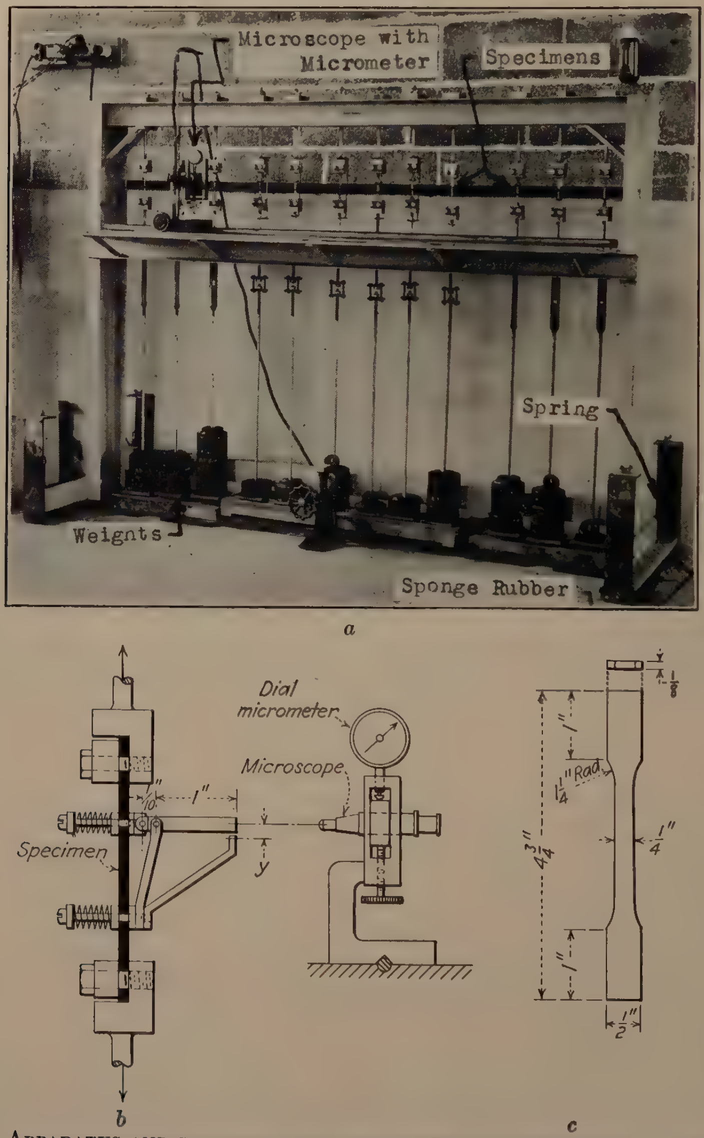

FIG. 4.—APPARATUS AND SPECIMEN FOR CREEP TESTS OF SINGLE-CRYSTAL SPECIMENS.
a. Test rack for creep tests under long-continued steady load.
b. Extensometer used to measure creep.
c. Tensile specimen for creep tests, fatigue tests and short-time tensile tests, with tip cut off.

plane, the shape of the interference spot will be altered. Radial lengthening on the pattern of a Laue interference spot is called "asterism," and the distortion of the plane reflecting surface may be due to: (1) reorientation of the approximately unidirectional grains, which appear to form a single crystal, (2) dislocation of these grains, and (3) random fragmentation of certain of these grains, the changes becoming more pronounced as the deformation of the crystal as a whole increases.* If the Laue spots are free from "fuzziness" the crystal is sometimes said to be "strain-free," although the term "strain" as used here indicates any distortion or disarrangement of the normal crystal structure, rather than the percentage of elongation or shortening.

Apparatus

Creep-test Apparatus and Technique.—The ratio of maximum resolved shear stress to direct tensile stress was computed for each of 12 single-crystal specimens. The specimens were so loaded that a series of creep tests under resolved shear stresses of varying magnitude was carried out. The specimens were placed in a creep-test rack (Fig. 4*a*). An aluminum extensometer was clamped to each specimen over a 1-in. gauge length. The motion of the movable arm of the extensometer was measured by a microscope focused successively on a witness mark on the fixed and another on the movable arm of the extensometer (Fig. 4*b*).† The microscope was moved vertically by means of a screw to permit this focusing, and the motion was measured by means of a micrometer dial gauge. Elongation could be measured to 0.0001 inch.

At intervals during a creep test a specimen was removed from the test rack for examination under a microscope for slip lines, for examination by X-rays to detect changes in the Laue pattern, and for determination of reorientation by means of the reflection method.

Apparatus for Tensile Tests and for Fatigue Tests.—For short-time tensile tests there was used a machine with a pendulum weighing apparatus and a maximum load capacity of 1000 lb. with lever adjustments for smaller ranges of load. The speed of the pulling head of the machine was 0.026 in. per minute. With the lever adjustment used, the load during a test could be read to 0.1 lb. For fatigue tests an axial-stress fatigue machine was used.‡ This machine applied 1000 cycles of stress per minute to a specimen, 1,500,000 cycles of stress per day of 24 hr. The magnitude of the load was measured by the deflection of an elastic ring, and the ring used in these tests showed a deflection of 0.0006 in. for 1-lb. load on the specimen. The deflection of the spring was measured by means of a micrometer dial gauge. The range of stress applied during a cycle to the fatigue specimens was from zero to a maximum tensile stress.

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* Explanation suggested by Dr. H. J. Gough.

† A fuller description of the extensometer is given in reference 8.

‡ For fuller description of the fatigue machine used in these tests see reference 9.

LATTICE ORIENTATION CHANGES DURING CREEP TESTS

Two single-crystal specimens, crystal No. 2 and crystal No. 7, show the two characteristic types of change of space-lattice orientation shown in the creep tests, and the test results for these two crystals are given in Table 1. From the light-reflection test results there were computed the orientation of the crystal and the resolved shear stress along the three slip directions: (1) before the test, (2) after 1000 hr. under load, and (3) after 2000 hr. under load. As the orientation angle of the specimen with refer-

TABLE 1.—*Resolved Shear Stresses, Pounds per Square Inch*

Octahedral Plane	Stress	Crystal No. 7			Crystal No. 2			Crystal No. 24
		Initial	After 1000 Hr. Creep	After 2000 Hr. Creep	Initial	After 1000 Hr. Creep	After 2000 Hr. Creep	Initial
(111)	S_{12}	14	254	254	*148*	133	158	256
	S_{13}	197	8	8	4	44	18	76
	S_{14}	*256*	228	*283*	141	165	152	334
$(1\bar{1}1)$	S_{21}	15	221	222	146	144	162	*350*
	S_{23}	218	*273*	257	146	151	152	302
	S_{24}	175	49	35	2	10	12	88
$(\bar{1}\bar{1}1)$	S_{31}	89	6	6	4	41	20	94
	S_{32}	91	256	223	143	129	148	271
	S_{34}	192	225	228	139	*167*	158	300
$(\bar{1}11)$	S_{41}	110	220	245	143	147	*166*	300
	S_{42}	70	55	34	2	8	12	58
	S_{43}	183	266	261	147	160	155	219
AREAS OF OCTAHEDRAL PLANES, SQ. IN.								
(111)		0.0384	0.0394	0.0386	0.0460	0.0439	0.0488	
$(1\bar{1}1)$		0.0358	0.0453	0.0441	0.0468	0.0405	0.0426	
$(\bar{1}\bar{1}1)$		0.0851	0.0483	0.0509	0.0478	0.0474	0.0437	
$(\bar{1}11)$		0.0886	0.0409	0.0446	0.0453	0.0493	0.0445	
DIMENSIONS OF CROSS SECTION OF SPECIMEN, IN.								
Width..................		0.255	0.241	0.236	0.260	0.253	0.253	
Thickness..............		0.125	0.123	0.123	0.125	0.123	0.120	
Applied tensile load, lb...				18.0		11.5		
Tensile stress over cross section..............				563		354		

ence to the specimen axis changes, the areas of the octahedral planes across the specimen also change, and from the change of these areas any change of orientation can be computed. For both crystal No. 2 and crystal No. 7, as creep progresses, the areas of the octahedral planes changed appreciably, indicating a distinct change in orientation of the crystal. Some twist of the crystal was noted.

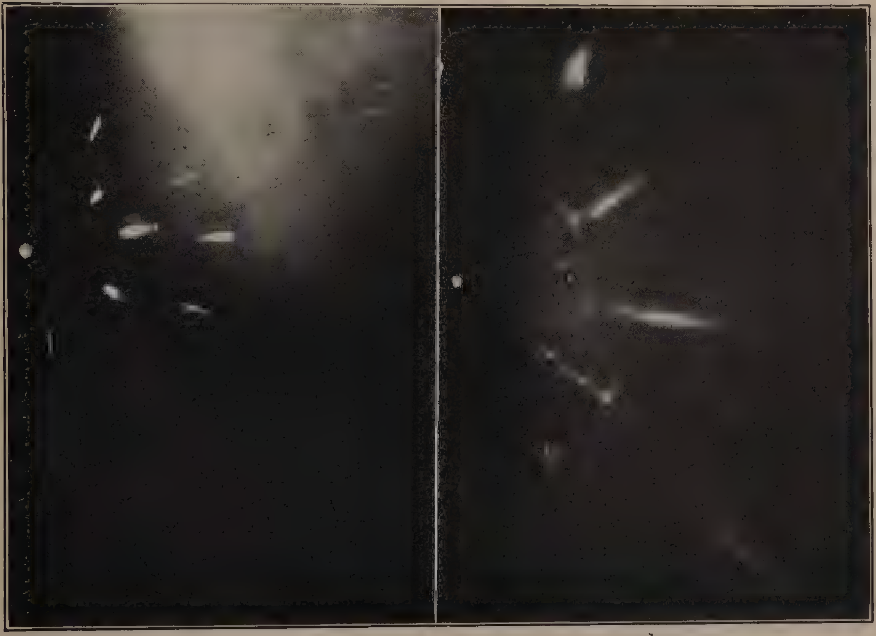

FIG. 5.—X-RAY PATTERNS OF CRYSTAL NO. 2.
a, initial Laue pattern; *b*, Laue pattern after 2600 hr. under steady load.

"BALANCED" STRESS AND "DOMINANT" STRESS

In the crystal No. 7 at the beginning of the creep test there was on the (111) plane a well marked maximum resolved shear stress, S_{14}. This well marked maximum stress will be called a "dominant" stress. After 1000 hr., however, there had been a considerable readjustment of the stress system on this plane, the stress S_{13} becoming almost negligible, while the stresses S_{12} and S_{14} became larger and more nearly equal. After 2000 hr. the difference between S_{12} and S_{14} was greater than at 1000 hr., but there was no stress so much greater than any other as to deserve the name "dominant." The same kind of readjustment of stress system with time can be noted on the other octahedral planes of crystal No. 7.

The original stress system in crystal No. 7 will be called "unbalanced," and the stress system developed during the reorientation process that accompanied creep will be called a "balanced" system, although the term "creep-resistant" might be preferred by some. Table 1 shows that the resolved shear-stress system in crystal No. 2 was practically "balanced" at the beginning of the creep test, and remained in balance, although there was some reorientation, as was shown by the changes in area of the octahedral planes. The other crystals subjected to creep test showed one or the other of these patterns of stress distribution. The tendency in all cases was to preserve or to develop a "balanced" stress system.

Examination under the microscope showed that crystal No. 7 developed slip lines within 200 hr., while no slip lines could be detected on crystal No. 2 even after 2000 hr. (magnification 200 ×). The different behavior of the two crystals can, it is believed, be explained as follows: In crystal No. 7 there was a "dominant" stress, which caused so great distortion in a given direction that the atomic bonds were temporarily broken and visible slip took place. However, as slip proceeded another stress may have become a slip-causing factor and slip may have begun in another direction. A series of slips alternating in direction may well have caused the slight twisting distortion that was present in the specimen after the completion of the creep test.

Crystal No. 2 exhibited creep, but no slip lines were visible in photomicrographs at 200 dia. magnification. It seems quite possible that the continuing elongation was accompanied by the formation of many small "crystallites" with orientation only slightly different from that of the original crystal—not enough disturbance of atomic structure to affect regions large enough to develop visible slip lines. The X-ray patterns are in harmony with this explanation. The X-ray pattern for the crystal before loading is shown in Fig. 5*a*. After 1000 hr. the Laue spots had become somewhat elongated. After 2000 hr. the spots were "fuzzy" and elongated. After 2600 hr. (Fig. 5*b*) the spots had developed "beads" and incipient "powder rings." The beads are indicative of many small crystallites with nearly the same orientation as the original crystal structure. As the structure became distorted because of the applied load, the strain was probably relieved by these crystallites. As the distortion continued, the crystallites took up orientations still farther out of line with that of the mother crystal, and "powder rings" started to form, indicative of random orientation. In contrast with the X-ray pattern of crystal No. 2, the pattern of crystal No. 7 showed evidence of relatively slight structural disturbance until after 2000 hr., when the stress system had become somewhat "balanced."

CREEP DIAGRAMS FOR SINGLE CRYSTALS

Fig. 6 shows typical creep-time diagrams for four single-crystal specimens tested under four different resolved shear stresses, and Fig. 7

shows a comparison between creep of two single-crystal specimens and two multicrystal specimens cut from the same sheath that furnished the metal for the single-crystal specimens. Since the maximum resolved shearing stresses for the myriad different crystalline grains of the multicrystal specimens are in different directions and of different amounts, it is not feasible to use resolved shearing stress for comparing creep of single and multicrystal specimens, and in Fig. 7 the average tensile stress (load divided by area of cross section) is used instead. The creep-time curves are not so smooth for the single crystals as for the multicrystal specimens; possibly this is due to the passing at intervals of governing resolved shear stress from one direction to another in the single crystals, and to continuing steady creep at grain boundaries of the multicrystal specimens. In general, for the test stresses reported, the creep of the single-crystal specimens for a given stress would seem to be somewhat *less* than that of the

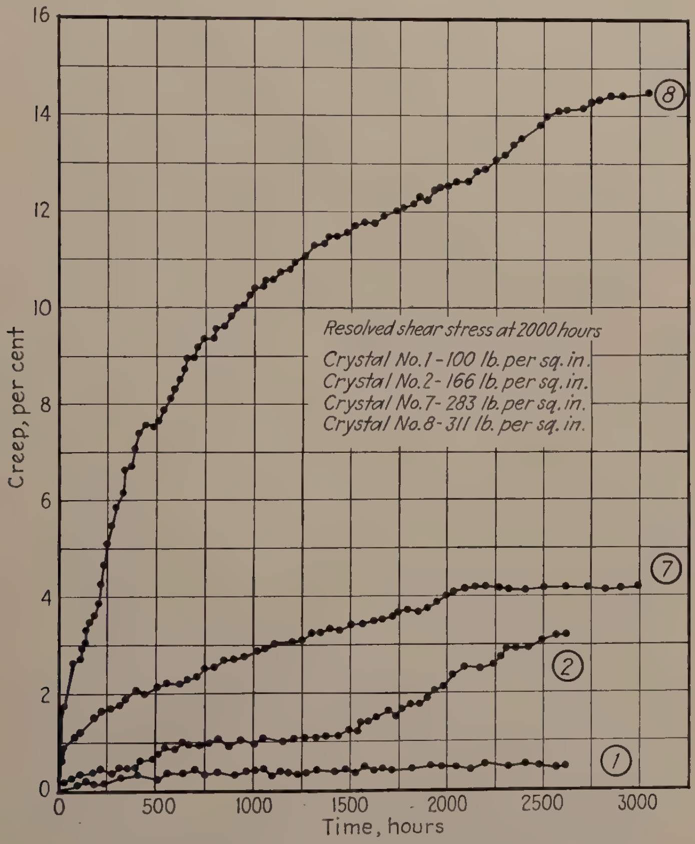

FIG. 6.—CREEP-TIME DIAGRAMS FOR SEVERAL CRYSTALS.

multicrystal specimens, but no general conclusion to this effect should be drawn from so few test results. With the possible exception of crystal No. 2 the shape of the creep-time diagrams for single crystals seems to be similar to that for creep-time diagrams for multicrystal specimens (see Figs. 6, 7 and 10). It may be noted that crystal No. 2 showed a "balanced" stress system from the very start of the creep test, and hence the chance of somewhat irregular changes of ruling resolved shear stress and of slip direction might not be unexpected. Crystal No. 24 (Fig. 10) shows clearly the typical three stages of creep (initial *OA*, steady *AB* and accelerated with "necking down" *BC*).

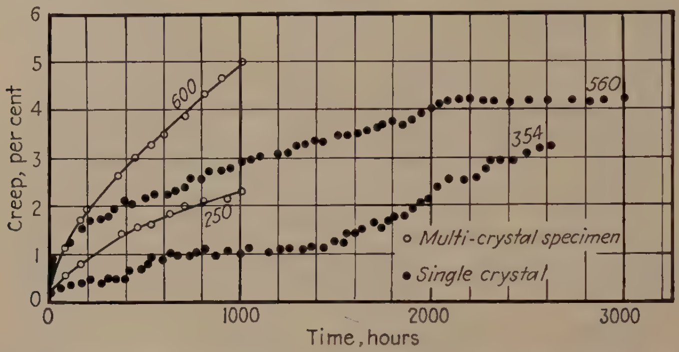

FIG. 7.—CREEP-TIME DIAGRAMS FOR SINGLE-CRYSTAL SPECIMENS AND FOR MULTICRYSTAL SPECIMENS.

The figures on each diagram give the tensile stress in pounds per square inch. The multicrystal specimens and the metal for making the single-crystal specimens were cut from the same piece of unusually pure grade I lead sheathing.

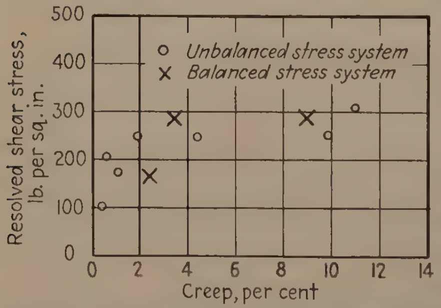

FIG. 8.—RELATION BETWEEN CREEP AT 2000 HOURS AND MAXIMUM RESOLVED SHEAR STRESS AS COMPUTED AT 2000 HOURS.

In Fig. 8 the percentage creep of the various single crystals after 2000 hr. under load has been plotted against the maximum resolved shearing stress determined also after 2000 hr. under load. Specimens that showed visible slip lines are designated by *o* and those with "balanced" stress systems (which showed no slip lines) are designated by *x*. From the results shown in Fig. 8, it would seem that a resolved shear stress of about 250 lb. per sq. in. might be taken as an arbitrary limiting value for single crystals of the lead tested, below which creep would be slight and above which it would be considerable. Possibly the creep limit for the "balanced" crystals would be a trifle higher than this.

CREEP TO FRACTURE UNDER CONSTANT LOAD

Five single-crystal specimens were tested to fracture under steady load. These specimens were not removed from the test rack during the test (mainly on account of the short time the specimens were under test), and hence the changes in orientation were not determined. Fig. 9 shows graphically the elongation at fracture for these five specimens. Percentage of elongation at fracture diminished somewhat with the time necessary for fracture. The fractures of all the specimens were chisel-shaped, and the elongations in 2 in. ranged from 40 to 58 per cent.

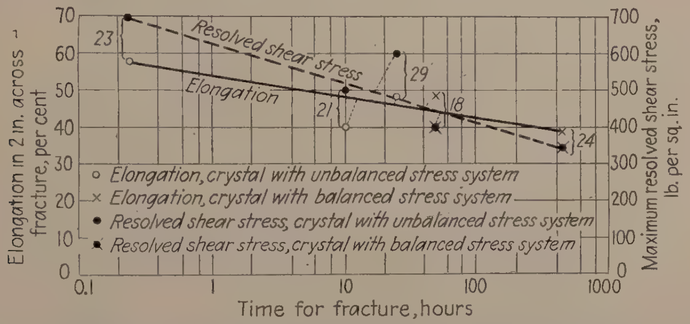

FIG. 9.—ELONGATION AT FRACTURE AND MAXIMUM RESOLVED SHEAR STRESS FOR SEVERAL CRYSTALS UNDER LONG-TIME STEADY LOAD.
Numbers refer to laboratory numbers assigned to single-crystal specimens.

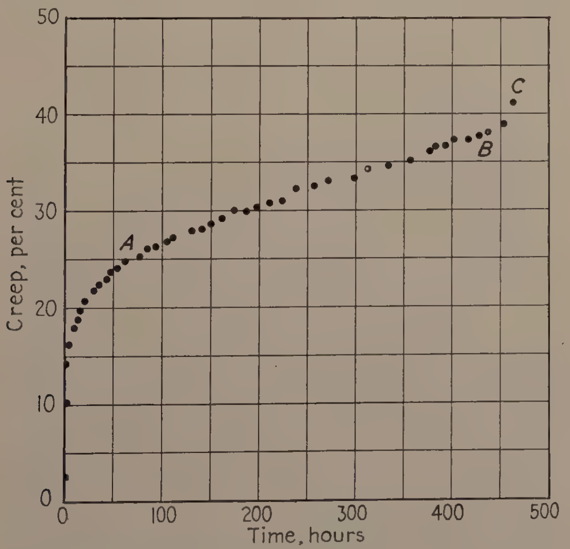

FIG. 10.—CREEP-TIME DIAGRAM FOR CRYSTAL NO. 24.
Initial maximum resolved shear stress 350 lb. per square inch.

The creep-time curve for crystal No. 24 may be taken as a typical creep-time curve to fracture for a single crystal. In this crystal the initial stress system was only fairly well "balanced" (Table 1), therefore rearrangement to a more perfectly "balanced" system may be expected. The time-creep diagram, Fig. 10, is similar in general shape to such diagrams for multicrystal specimens of lead, and consists of three fairly well defined stages: (1) a stage of rapid preliminary creep (*OA* in Fig. 10), (2) a relatively long stage of creep at an approximately constant rate (*AB* in Fig. 10), and (3) a rapid stretch to fracture (*BC* in Fig. 10).

The following explanation is offered: During the first stage slipping and reorientation toward a more "creep-resistant" stress system take place; during the second stage a "balanced" (more creep-resistant) stress system has been set up, and creep continues at a diminished, and approximately constant, rate; during the third stage dislocation and fragmentation have become so pronounced that creep rate is accelerated, and a progressive fracture develops.

In the immediate vicinity of the fracture of crystal No. 24 large crystals with random orientation were visible to the unaided eye. Fig. 11 is a Laue pattern about ½ in. from the fracture, and it indicates that the original structure of the crystal was not entirely destroyed, although badly distorted. Probably there had been some stress relief due to the formation of small crystallites with orientation quite close to that of the mother crystal. The width of the powder-ring fragments indicates that these crystallites were of small size. This Laue pattern is not dissimilar to patterns for some of the low-load creep specimens, and this suggests that the mechanism that causes fracture under steady load is an intensification of the mechanism that acts during the early stages of creep.

FATIGUE-TEST RESULTS

One series of five single-crystal specimens was tested under repeated axial tensile stress (range zero to maximum). Table 2 shows the results of these tests.

TABLE 2.—*Results of Repeated Tension Tests of Crystals*

Crysta	Initial Maximum Resolved Shear Stress, Lb. per Sq. In.	Cycles of Stress for Fracture, 1000 Cycles per Min.	Elongation in 2 In. at Fracture, Per Cent
25	300	2,400,000	37.2
22	250	3,637,000	24.5
27	225	2,384,900	15.1
13	200	26,000,000 no fracture	
20	150	32,000,000 no fracture	

Specimen No. 20 was subjected to an initially "unbalanced" stress system with a maximum resolved shear stress of 150 lb. per sq. in. After

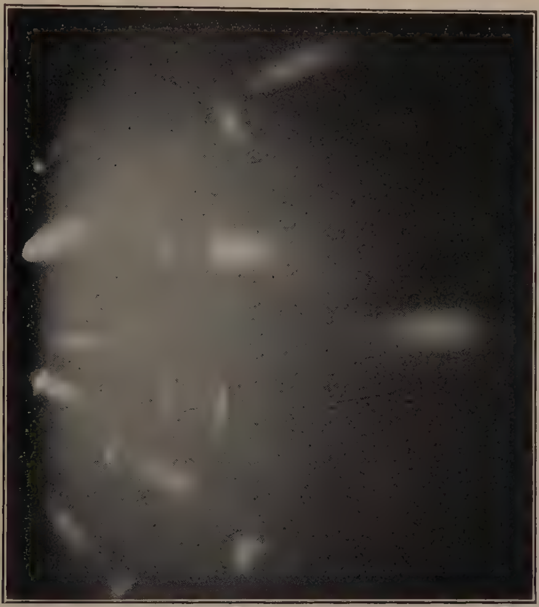

FIG. 11.—X-RAY PATTERN OF CRYSTAL NO. 24 TAKEN ABOUT ONE-HALF INCH FROM FRACTURE.

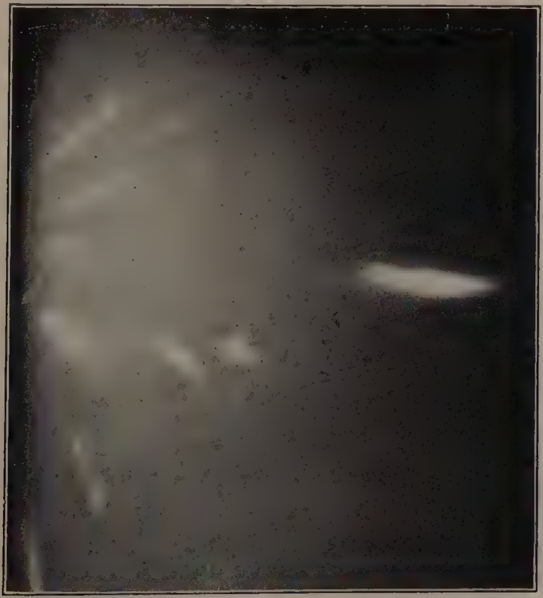

FIG. 12.—X-RAY PATTERN OF CRYSTAL NO. 20 AFTER TWENTY MILLION CYCLES OF TENSILE STRESS.

20,000,000 repetitions of stress, the specimen was found to be reoriented so that the stress system was practically "balanced." Slip lines had appeared after 5,000,000 repetitions. The X-ray pattern after 20,000,000 repetitions (Fig. 12) showed that there was considerable distortion in the crystal lattice, and several spots had developed "beads" indicating the formation of crystallites. The specimen sustained 32,000,000 repetitions before it was removed from test. The X-ray pattern, however, showed that the structure was badly distorted with some evidence of powder rings forming, and it is quite likely that eventually failure would have occurred.

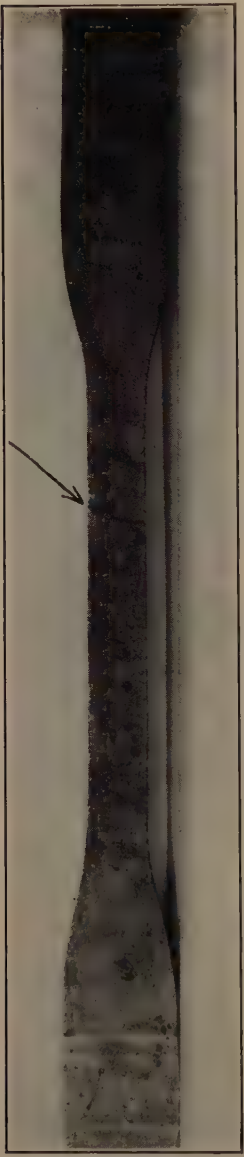

Fig. 13.—Fatigue crack developing in single-crystal specimen No. 27.

Crystal No. 27 was subjected to an "unbalanced" stress system with a maximum resolved shear stress of 225 lb. per sq. in. The initial data suggested that slip would take place on the (111) plane at an angle of 69° with the edge of the specimen. Slip was present after 1,000,000 repetitions, and the measured angle was 70°. The X-ray pattern showed considerable distortion in the crystal structure. After 2,369,700 repetitions it was noticed that the specimen was developing a crack (Fig. 13). The X-ray pattern taken in the region just to the right of this crack (Fig. 14) showed that the structure had been so badly distorted that fracture seemed imminent, although the original single crystal was still existent. The specimen was replaced in the testing machine and sustained only 16,200 further cycles of stress before fracture. The X-ray pattern at the fracture (Fig. 15) showed that there was still evidence of the original zone of spots, but they had become very feathery. At the same time the pattern is spotted with new random specks indicating the production of rather large random-oriented crystals. Many crystallites may also have formed on the crystal planes; since some spots have developed the "beads" indicative of their presence.

There are insufficient data from which to draw definite conclusions as to any "endurance limit" for single crystals of lead. About all that can

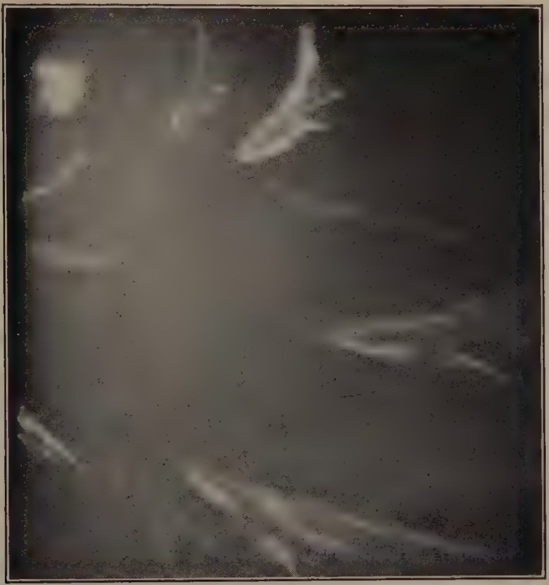

FIG. 14.—X-RAY PATTERN TAKEN JUST TO RIGHT OF FATIGUE CRACK IN CRYSTAL No. 27.

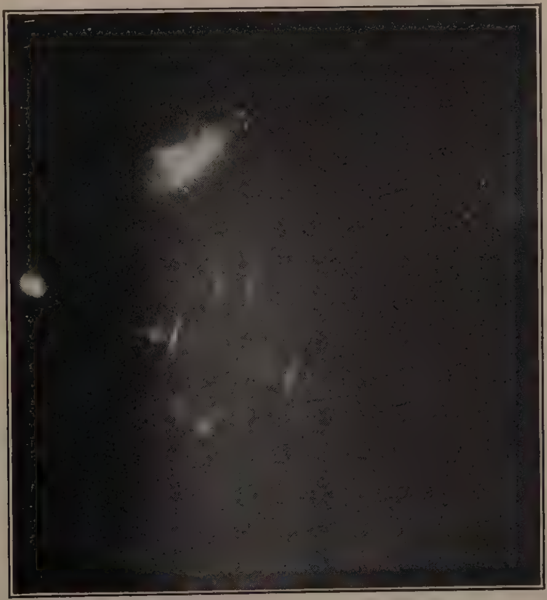

FIG. 15.—X-RAY PATTERN TAKEN AT BREAK AFTER FRACTURE OF CRYSTAL No. 27.

be said is that under cycles of resolved shear stress of 250 lb. per sq. in., or more, single crystals of lead failed relatively rapidly.*

Fracture occurred without appreciable necking-down of the specimen, the path of fracture following a slip line. The direction of fracture under repeated stress, like the direction of slip lines, followed, then, the direction of maximum resolved shear stress along the intersection of two octahedral planes of the crystal. In creep tests to fracture the elongation across fracture was over 40 per cent in a gauge length of 2 in. Under repeated tension the elongation was smaller than this value, and was smaller for long tests under low stress than for shorter tests under relatively high stress. In the fatigue tests there seems to have been an interference with the development of full elongation. It is suggested that this "interference" may be associated with the "beads" found in the X-ray pattern of the structure just previous to fracture. The beads indicate the formation of crystallites along atomic planes with an orientation only slightly different from that of the original crystal, and evidences of such crystallite formation were found to be more abundant in the X-ray patterns for repeated-stress specimens than in creep-test specimens. The formation of such crystallites may facilitate the formation of cracks without permitting a high degree of elongation of the specimen as a whole.

Short-time Tensile Tests

One series of single-crystal specimens was subjected to ordinary short-time tensile tests in the testing machine previously described. In all such tests it was found that stretch proceeded slowly until a maximum resolved shear stress of approximately 250 lb. per sq. in. was developed, after which the elongation became much more rapid. Fracture occurred at a resolved shear stress of approximately 700 lb. per sq. in. and with an elongation of from 40 to 50 per cent in 2 in. These results are in harmony with results obtained in the long-time creep tests.

Conclusions

By means of room-temperature creep tests of single-crystal specimens cast from the metal of a sheath of unusually pure commercial lead, an empirical critical resolved shear stress of approximately 250 lb. per sq. in. was determined. Any stress above this caused relatively rapid creep in the single-crystal specimens. In short-time tensile tests on a testing machine elongation increased at an accelerated rate above this stress. In repeated-tension fatigue tests this critical resolved shear stress marked approximately a boundary below which specimens withstood without fracture some 30,000,000 cycles of stress and above which they withstood less than 4,000,000. This critical resolved shear stress seems to be an important, even though empirical, strength constant of single crystals of this metal at room temperature.

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* Speed of repetition of test has been found to be a major factor in determining endurance limit[2] of lead.

The general similarity between the shape of the creep-time diagrams for single crystals of lead and the shape of creep-time diagrams for multicrystal specimens of the same lead offers a strong indication that the creep of ordinary commercial multicrystal lead takes place largely on account of the overcoming of the creep-resistant properties within the grains. It is to be expected that the creep will be modified to some extent by grain-boundary restraints, and, while it is not safe to draw general conclusions, the tests herein reported suggest that continuous creep at grain boundaries seems to make creep-time diagrams smoother for multicrystal specimens than for single crystals, and that creep at grain boundaries may well cause distortion, which adds to the total creep of a specimen, so that single crystals under a given stress may actually creep slightly less in a given time than do multicrystal specimens of the same metal.

From short-time tension tests the ultimate resolved shear stress for single crystals was found to be about 700 lb. per sq. in. Fracture occurred after an elongation of from 40 to 50 per cent. Creep tests to fracture developed slightly less elongation, but under repeated tension tests (zero to maximum tensile stress) developed much smaller elongation at fracture. In the repeated-stress tests the Laue X-ray patterns gave indication of the formation of crystallites on atomic planes, which seemed to inhibit, or at least curtail, elongation. Repeated loading seemed to cause a fracture to start, and, once started, to spread so rapidly under repeated stress that, in spite of accelerated creep *rate*, the specimen broke in two before there had occurred as much *total* elongation as would take place under a steady load to fracture. This was especially true for crystals tested under cycles of repeated stress with low maximum stress. Further detailed study of the second and third stages of creep under repeated stress seems very desirable.

During creep tests of single crystals of lead there was observed a twist of the specimen, apparently accompanying the reorientation of the crystal structure which increased its resistance to creep. The result of the reorientation seems to be the tendency towards a kind of equilibrium or "balance" by which two of the three resolved shear stresses on any octahedral plane become nearly equal, while the third becomes small in magnitude.

If the original orientation of the crystal structure causes one of the three resolved shear stresses on an octahedral plane to be a "dominant" stress, considerably larger than the other two, then slip takes place along that plane in the direction of the dominant stress. However, slipping causes a readjustment and that stress may cease to be dominant, and then slip in that direction ceases, while slip occurs in the direction of one of the other stresses which has become dominant. Successive slip stages occur until a balanced stress system is reached. Further distortion seems to be accompanied by the formation of crystallites of increasing heterogeniety of orientation, and finally by actual spreading cracks.

Some evidence was seen that seemed to indicate that slip in a crystal with an originally "balanced" shear-stress system occurs without the formation of visible slip lines. Possibly slip lines might have been seen under higher magnification than that used.

In every crystal in which fracture occurred there was evidence of recrystallization of the specimen in the region near to the fracture. Newly formed small grains were visible to the unaided eye, but they were not formed far from the break. The region near the fracture is very severely distorted, and the shock of fracture may be sufficient to cause this recrystallization. Localized heat effects at the fracture may also be a contributing factor in this recrystallization.

Acknowledgment

The help of the following persons and firms is gratefully acknowledged: Prof. G. L. Clark, of the University of Illinois, who made available the facilities of the X-ray laboratory and gave valuable assistance in the X-ray studies; Mr. C. W. Dollins, engineer of tests with the Investigation of Creep and Fracture of Lead Sheathing, who gave valuable assistance in preparing specimens and making tests; The Commonwealth Edison Company of Chicago, which furnished the very pure lead. Thanks for criticism and suggestions are given to Dr. H. J. Gough, of the British National Physical Laboratory; Mr. W. A. Cowan, of the National Lead Co.; Mr. C. H. Greenall, of the Bell Telephone Laboratories; Prof. M. Gensamer, of the Carnegie Institute of Technology; and Prof. C. H. Mathewson, of Yale University.

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APPENDIX I.—*Orientation Data*

The polar coordinates of the "reflection spots" obtained by orientation sphere
λ is latitude measured from equatorial great circle
μ is longitude measured from plane perpendicular to center of wide face of specimen

Octahedral Plane	Stress	Crystal No. 7						Crystal No. 2					
		Initial		After 1000 hr.		After 2000 hr.		Initial		After 1000 hr.		After 2000 hr.	
		λ	μ	λ	μ	λ	μ	λ	μ	λ	μ	λ	μ
(111)		56°	W17°	49°	W8°	45°	W6°	45°	E26°	45°	E10°	40°	E13°
$(1\bar{1}1)$		63°	E157°	41°	E86°	46°	E91°	44°	E113°	50°	E109°	45°	E105°
$(\bar{1}\bar{1}1)$		22°	W143°	38°	E168°	35°	E179°	43°	W156°	41°	W153°	44°	W159°
$(\bar{1}11)$		21°	W78°	47°	W108°	39°	W98°	46°	W66°	39°	W75°	43°	W70°
Axis of specimen (computed)		71°	W104°	84°	E147°	84°	W125°	89°	W157°	84°	W89°	89°	W38°

ANGLE BETWEEN RESOLVED SHEER STRESS DIRECTIONS AND AXIS OF SPECIMEN

(111)	S_{12}	88°	56°	56°	54°	59°	53°
	S_{13}	65°	89°	89°	89°	80°	85°
	S_{14}	57°	60°	52°	56°	51°	50°
$(1\bar{1}1)$	S_{21}	88°	56°	56°	54°	59°	53°
	S_{23}	64°	46°	51°	53°	57°	55°
	S_{24}	69°	82°	85°	89°	88°	87°
$(\bar{1}\bar{1}1)$	S_{31}	65°	89°	89°	89°	80°	85°
	S_{32}	64°	46°	51°	53°	57°	55°
	S_{34}	25°	52°	50°	54°	46°	53°
$(\bar{1}11)$	S_{41}	57°	60°	52°	56°	51°	50°
	S_{42}	69°	82°	85°	89°	88°	87°
	S_{43}	25°	52°	50°	54°	46°	53°

DISCUSSION

(*Norman B. Pilling presiding*)

C. S. BARRETT,* Pittsburgh, Pa. (written discussion).—Some conclusions in this paper that the authors have drawn from X-ray patterns appear to be somewhat misleading and should, I think, be modified. In several places the authors refer to

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* Metals Research Laboratory, Carnegie Institute of Technology.

"beads" on asterism streaks in the Laue patterns and seem to attach some special significance to them relative to the deformation process and to the amount of elongation of specimens during fatigue. If these beads are the ones visible in Figs. 11, 12 and 15, it is not necessary to delve into the deformation process to find their significance, for they are merely the K_α and K_β spectra from the molybdenum target; each asterism streak is a partial or a complete spectrum of the incident radiation, and the intense characteristic lines of this radiation cause the "beads." To put it another way, the beads are segments of Debye rings.

Regarding Fig. 12 and the fatigue specimen to which it relates, the following statement is made: "The X-ray pattern, however, showed that the structure was badly distorted with some evidence of powder rings forming, and it is quite likely that eventually failure would have occurred." Probably the authors did not intend to convey the impression that X-rays can predict, in general, whether or not a specimen will eventually fail in fatigue, but the sentence is likely to mean that to some people, and I should like to do what I can to prevent this interpretation. Plastic flow in fatigue specimens has frequently been observed with stresses below the endurance limit. In all materials where this is possible, the X-ray patterns may be expected to change without indicating damage to the material. Experiments previously reported by the authors have indicated that there is no definite endurance limit for lead; that is, no stress below which fracture will not eventually occur if stressing is continued long enough. So perhaps the statement I am objecting to is justified for lead, in the sense that the X-ray patterns show that *some* stress has been applied, and *any* stress applied will eventually lead to failure. But the point I wish to emphasize is that the X-ray patterns do not register damage to the material; they merely register certain results of plastic flow at the spot where the rays happen to fall, which may or may not be the spot where a crack will eventually form. Without exhaustive experiments covering a given set of conditions for a given metal, X-ray patterns can give no assurance that a damaging state of stressing will be detected, or that what appears damaging may actually be so.

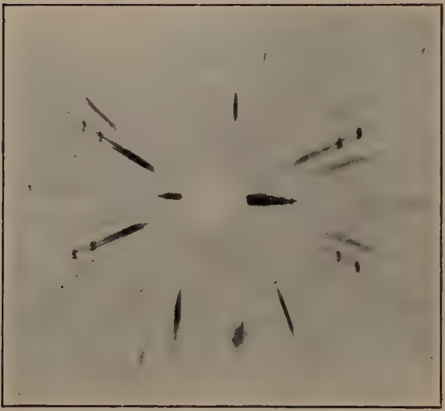

FIG. 16.—ASTERISM CAUSED BY BENDING SINGLE CRYSTAL OF SILICON STEEL INTO SEGMENT OF CYLINDER.

Perhaps a photograph would clear up the matter of "beads" still further. Fig. 16 shows asterism caused by bending a single crystal of silicon steel into a segment of a cylinder. Molybdenum radiation collimated by a pinhole system was transmitted through the bent ferrite crystal to form the pattern. The K_α and K_β spectra appear crossing certain streaks, and it will be noted that these characteristic lines have the same width as the streaks, which is not true of the "beads" of Figs. 11, 12 and 15. There can be no doubt, I think, that in this bent ferrite specimen the orientations fill a range about a single axis of deformation, while in the lead specimens the axes of bending or rotation are numerous. The diffraction spots from the lead spread laterally as well as longitudinally, remaining most intense near the center of each streak and decreasing in intensity on each side, giving a fuzzy appearance to each streak. (For a discussion of similar distortion produced by fatigue and by static stressing in polycrystalline iron see C. S. Barrett: *Metals and Alloys*, January 1937.) Under these conditions it is clear that the stronger the exposure, the wider the streaks will appear on the film, and at the place where the intense K_α and K_β lines fall, the streaks will appear much wider than elsewhere, producing the appearance described by the authors as "beads."

A. J. Phillips,* Barber, N. J. (written discussion).—From the data given in the Appendix, I have worked out stereographically the orientation of the two crystals referred to in Table 1 on page 124. In Fig. 17 are plotted the "initial" reflection planes of crystal No. 7, while in Fig. 18 those for crystal No. 2 are shown.

In the stereographic projections the four planes are labeled with the same Miller indices as those given in the paper and differ slightly from the usual convention.

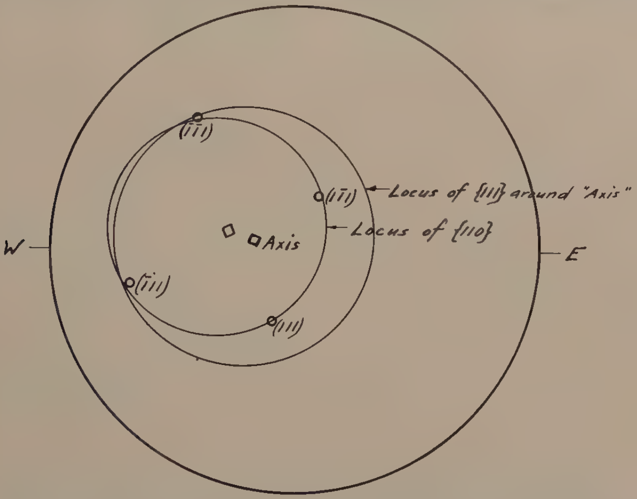

Fig. 17.—Stereographic projection of poles of reflection planes of crystal 7.

With regard to crystal No. 2 (Fig. 18) I find, upon describing a small circle around the "axis" with a radius of 54° 44′, which should be the locus of all {111} planes, that none of the four points plotted fall on this circle. However, when a small circle with a radius of 45° is described around the axis all four of the plotted points fall within one degree of the circle. This is, of course, characteristic of {110} planes. Likewise, the angular distances from one point to another, as determined by means of Wulff nets, are given in Table 3. These angular distances are within 3° at the most and average within 1° of the typical angular distances for {110} planes.

Table 3.—*Angular Distances Determined by Wulff Nets*

Planes	Crystal No. 7	Crystal No. 2
(111) to $(1\bar{1}1)$	61°	59°
$(1\bar{1}1)$ to $(\bar{1}\bar{1}1)$	57°	63°
$(\bar{1}\bar{1}1)$ to $(\bar{1}11)$	60°	61°
$(\bar{1}11)$ to (111)	57°	61°
(111) to $(\bar{1}\bar{1}1)$	90°	92°
$(1\bar{1}1)$ to $(\bar{1}11)$	86°	90°

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* Superintendent of Research, Central Research Laboratory, American Smelting and Refining Co.

Crystal No. 7 shown in Fig. 17 is not quite as satisfactory as crystal No. 2. In the first place, the location of the crystal axis given in the paper is off several degrees, as is shown by the failure of the small circle with a radius of 54° 44′ to be even concentric with respect to the so-called {111} planes. However, when the axis is relocated and a small circle with a radius of 45° is described, the plotted points fall reasonably close to the circle and show the usual relationship for {110} planes, the worst error being 4° and the average error being less than 1½°.

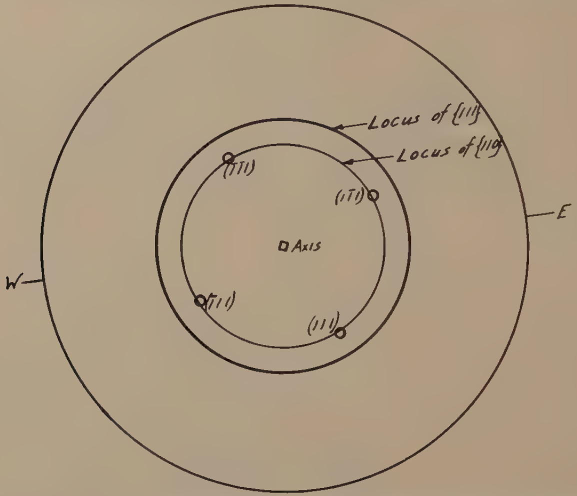

FIG. 18.—STEREOGRAPHIC PROJECTION OF POLES OF REFLECTION PLANES OF CRYSTAL 2.

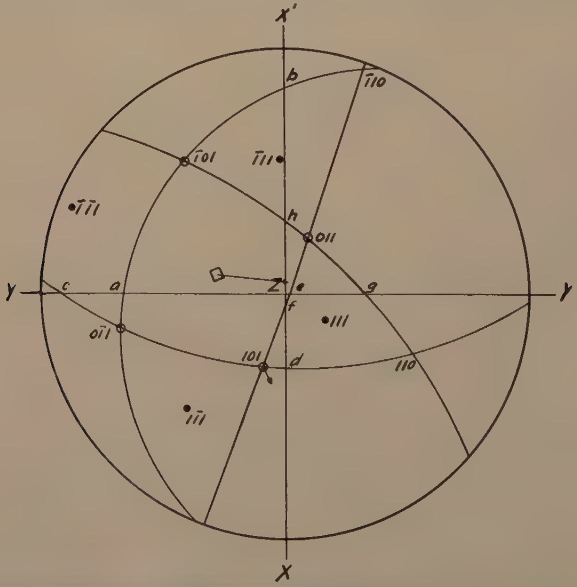

FIG. 19.—STEREOGRAPHIC PROJECTION OF RELOCATED {111} AND {110} IN CRYSTAL 7.

I have also worked out the orientation of both crystals from the data "After 1000 hr. Creep" and "After 2000 hr. Creep" and find that in every case the average location of the various points is within 3° of the characteristic position for {110} planes and could not possibly represent {111} planes. It is thus evident that the etching technique employed by the authors of this paper developed the reflection facets of the {110} planes rather than those of the {111} planes which they assumed. If this is true the "resolved shear stress" data given in Table 1 are incorrect and the subsequent deductions and conclusions from these data must be modified.

In Fig. 19 I have plotted stereographically the orientation of crystal No. 7, with the points plotted from the data designated as {110} planes, and in addition have shown the poles and traces of the {111} planes. By means of a series of simple calculations it is possible to prove that, with the applied tensile stress and assuming that slip will take place on {111} planes, slip will take place primarily on the ($\bar{1}11$) plane and in the [101] direction. If this is so the [101] direction should tend to revolve toward the tensile axis of the specimen represented by the center of the stereographic circle. However, the short arrow from the (101) pole in Fig. 19 represents the alleged change in location of this pole due to 1000 hr. creep. This change is decidedly in the wrong direction.

The arrow drawn from the pole of the cubic axis and running nearly parallel to $Y'Y$ represents the alleged change in this axis likewise due to 1000 hr. creep. This change in orientation is startlingly large when it is observed from Fig. 6 that the extension in creep during that period was just under 3 per cent. Consequently, to check this point a calculation was made to determine the theoretical change in orientation of the crystal by 4 per cent extension (that due to 2000 hr. creep) in tension by slip on the ($\bar{1}11$) plane and in the [101] direction. This calculation showed that there should be a movement of only 1½° as manifested by a rotation of the [101] direction along a radius towards the center of the stereographic projection.

Obviously the error in determining the orientation is as large or larger than the total possible change in orientation by slip on ($\bar{1}11$) planes in the [110] direction. Therefore, the method is not satisfactory and the difficulty in reconciling the observed orientation change with theoretical slip is easily explained.

J. B. Baker, B. B. Betty and H. F. Moore (written discussion).—Dr. Barrett questions the significance we have placed upon the formation of the "beads" on the Laue spots of the X-ray patterns. In watching the *changes* in the X-ray patterns *during the progress of the distortion tests* it was noted that the smooth, elliptically shaped Laue spots first became fuzzy and elongated radially. Then there appeared a transverse widening of the Laue spots, which we have called a "bead." An example of these beads is indicated along the left border of Fig. 11. With continued distortion these beads increased in length and became incipient rings. A powder ring is an indication of random orientation.

To explain the development of the bead we have suggested the development of small crystallites with very slightly different orientation from the plane that caused the original spot. As the distortion increased these crystallites became more random in their orientation and the powder rings increased in length and number.

The specimen shown in Fig. 12, which we indicated might have gone to failure, had produced a series of X-ray patterns similar to other specimens that had gone to failure. It was not the intention of the authors to infer that the probable failure of a specimen under fatigue can be predicted by this means.

The discussion by Dr. Phillips is based upon the premise that we were not obtaining reflections from {111} planes but from the {110} planes. This possibility was considered at the time the experimental work was performed and measures were taken to insure that we were dealing with the octahedral planes. As pointed out by Dr.

Phillips, the "pole" of the {111} plane exists at an angle of 54° 44′ from the crystal axis. These "poles" of the {111} would coincide with their reflections on the transparent sphere. To check the relative positions of these reflection spots a template was prepared to compare the spots with the poles that should be produced by the {111} planes. Good agreement was always attained. It may be added that the angles made by slip lines on several of the specimens gave good agreement with the theoretically computed angles that the traces of the {111} planes should produce.

In view of the disagreement as to angles of orientation of single-crystal specimens, the angles and resolved shear stresses reported in this paper may require revision. This involves the question of limitations of precision of the Bridgman reflection method, and of the conclusions relative to "balanced" and "unbalanced" stress. However, the qualitative significance of the conclusions relative to limiting resolved shear stress, similarity of creep-time diagrams for single crystal and for multicrystal specimens, ultimate resolved shear stresses, and relative creep of single-crystal and multicrystal specimens is not affected. From a few computed values it seems probable that values of maximum resolved shear stress will not be very greatly changed.

Measurements of Internal Friction in Age-hardening Alloys with a Modified Torsion Pendulum Apparatus

By R. A. Flinn, Jr.,* Student Associate, and John T. Norton,† Associate Member A.I.M.E.

(New York Meeting, February, 1938)

A considerable number of experiments in recent years have definitely established the fact that the internal friction or mechanical hysteresis of a metal under cyclic stress is a property that is highly "structure sensitive." Because of this fact, it has been suggested that an observation of this property, which often is referred to as "damping capacity," might be a useful indicator of structural changes taking place when a metal or alloy is subjected to any of a number of metallurgical treatments.

Damping capacity is of interest to both engineer and metallurgist, but from a rather different point of view, and the information that each desires from such observations is of a different nature. The metallurgist is in search of various external indications of changes taking place in the interior of a metal; changes which are in themselves not directly observable. Even if the observed phenomenon cannot be explained in fundamental terms, it may be empirically related to certain characteristics of the material and prove of real value in research. Internal friction or mechanical hysteresis occupies such a position, and, although it is not well understood in terms of basic metallic theory, an observation of its changes can serve in a very useful capacity. Of course, there is nothing new in the measurement of damping, but the use of this property in metallurgical research constitutes a vast field, which has received all too little attention.

The present work is essentially of an exploratory nature in this field and is an attempt to evaluate the process as a research tool. The phenomenon of age-hardening was chosen as a typical example of a structural change and one method of measuring damping was examined in considerable detail.

METHODS OF MEASURING DAMPING CAPACITY

Many kinds of observations can be made upon a specimen subjected to a cyclic stress from which can be calculated the energy absorbed in

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Manuscript received at the office of the Institute Dec. 1, 1937.

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passing through a cycle. These have been discussed in detail by Föppl.[1] For the problem at hand, certain considerations enter into the choice of a proper method. For research on alloy systems, the specimen should not be too large and should be easily machined into the desired form. Because some alloys change rapidly even at room temperature, the method of test should be capable of being set up quickly and should require only a few minutes for the test. Temperature control, preferably over a considerable range of temperatures, should be included. Since many structures are altered by plastic deformation, the method of measurement must provide for an accurate adjustment of the amount of strain to which the specimen is subjected, and it should be possible to study a wide range of strains with the same apparatus. In work of this sort the absolute value of the damping is less important than a precise knowledge of changes that occur in damping.

With these limitations in mind, there are two among the several available methods of measuring damping that seem particularly suitable for the development of a laboratory tool. The first involves a vibrating system in which a particular amplitude can be created corresponding to the desired maximum stress and then the system allowed to vibrate freely. The decrement of this vibration with time is a measure of the mechanical hysteresis. This procedure permits the decrement to be measured over a wide range of strains in a single run. The best known example of this method is the torsion pendulum in which the specimen forms the elastic element. The second method involves a vibrating system of which the specimen is a part and which can be excited by an energy source of a continuously variable frequency. In the neighborhood of the natural frequency, the amplitude of the vibration passes through a sharp resonance maximum and the width of this maximum peak in terms of frequency is a measure of the damping.

The second method is particularly adapted to the study of small strains where the damping is practically independent of the magnitude of the strain. The resonance method involves a measurement over a range of amplitudes corresponding to a range of strains of 100 per cent. For large strains, where the damping changes vary rapidly with the magnitude of strain, it is desirable to determine the damping for a number of specific strain values, which cannot be done by the resonance method. Excitation of a specimen at resonance may be accomplished by electromagnetic, piezoelectric, or even mechanical means, as has been done by Quimby,[2] Wegel,[3] Förster[4] and others.

One must compromise on the magnitude of strain used in an investigation because at small strains the change in damping capacity will be much smaller than at strains approaching the limit of the elastic behavior of the material. Thus a much more refined technique and a reduction of the inherent losses in the measuring instrument is necessary. On the other hand, the use of higher strains involves the possibility of producing some permanent change in the specimen during the period of observation. In the study of age-hardening, a strain that would be quite safe for the hardened sample might introduce considerable change in the freshly quenched specimens. For this reason it seems desirable to have a method that will be capable of investigating a considerable range of strains without a serious loss of sensitivity. Probably two separate instruments will be necessary.

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[1] References are at the end of the paper.

A reasonable view of such a laboratory method would indicate a sensitivity that would cause the loss in the instrument to be less than one per cent of the hysteresis loss in the specimen. For specimens with high damping, this sensitivity is easy to obtain, but since the damping may vary by several orders of magnitude from one material to another, any sort of universal instrument would have to be designed for very low losses. No very satisfactory data are available at present upon which to estimate the losses in apparatus of this type.

Experiments with the Torsion Pendulum Apparatus

In the design of laboratory apparatus for general use, it is an axiom that the simplest method is usually the best. This probably had something to do with the choice of the torsion pendulum method for preliminary investigation. The Föppl-Pertz[1] or von Hydekampf machine, which has had considerable vogue for measuring damping capacity, was used as a model for the general design. This consists essentially of a heavy rectangular metal frame, in the lower limb of which the specimen is clamped. This specimen, which is similar to that used for tensile tests, projects upwardly and has an inertia bar attached to its upper end. When the inertia bar is given a slight twist and released, it oscillates as an inverted torsion pendulum with the specimen as the elastic element, and the decrement of this oscillation is a measure of the damping or mechanical hysteresis.

Experience with this machine indicated that it was not suited to the study of low-damping materials such as duralumin and beryllium copper, because of large energy losses in the instrument. One source of loss was the recording system in which a pen attached to the inertia bar made a record on a moving strip of paper. This was replaced by an optical system in which the only attachment to the inertia bar was a small mirror. The light beam made a record on a revolving drum, from which the amplitude of motion of the bar was measured.

Another large and very variable source of loss was the pivot that supported the upper end of the specimen and prevented any motion in bending. After many trials, an entirely new method was devised, which has proved entirely satisfactory. Two blocks, one on the inertia bar and the other on the frame, were connected by two pairs of thin, flat springs. Rotation of one block with respect to the other was permitted by the bending of the spring strips, but since the two sets were at right angles no translation was possible. The springs bend through a very small angle, are of very low-damping material, and their volume is negligible as compared with that of the specimen. Such a pivot system is necessary because the specimens are seldom quite straight after heat-treatment. Careful observations with and without this pivot on a truly straight sample have demonstrated that the damping introduced is certainly less than the experimental error on a single specimen (about 2 per cent).

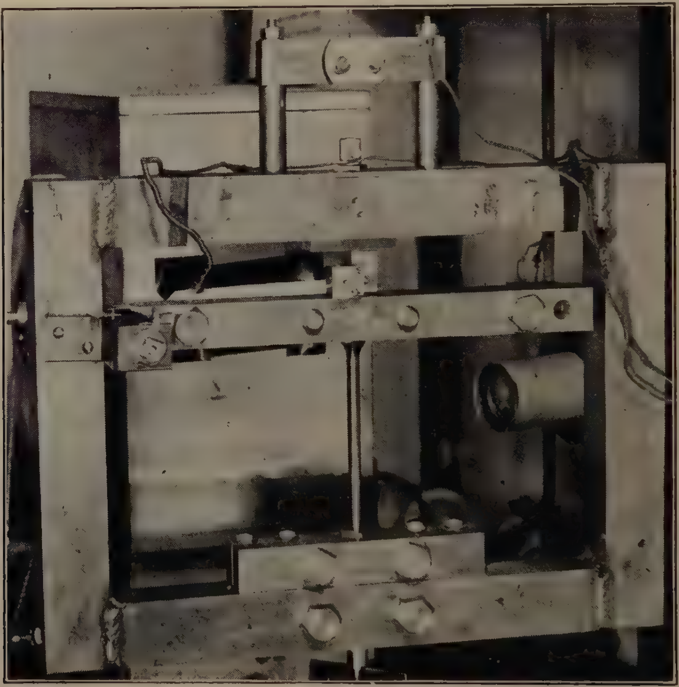

FIG. 1.—GENERAL VIEW OF TORSION PENDULUM UNIT, SHOWING ARRANGEMENT OF SUSPENSION, PIVOT, INERTIA BAR AND SPECIMEN.

Two other features of the Föppl-Pertz machine were retained and should be mentioned. One is the pair of electromagnets by means of which the inertia bar is twisted in order to stress the specimen at the start of the run. This arrangement permits starting without disturbance of the unit. The other is the method of suspension of the whole vibrating system, which consists of a single wire so that no energy can be transmitted to the surroundings. This method of suspension was rather troublesome, because of the motion of the vibrating unit as a whole with respect to the recording drum. After considerable practice it was found possible to bring the system very nearly to rest before releasing the inertia bar. Figs. 1 and 2 show the general setup of the apparatus and the detail of the pivot system.

METHODS OF EXPRESSING DAMPING CAPACITY

Several methods of expressing the damping capacity have been employed in the literature, and it is well to outline the method used here. With the torsion pendulum type of apparatus, a record of amplitude is obtained as a function of the number of cycles from some arbitrary starting point. The quantity frequently employed is the logarithmic decrement, which is the natural logarithm of the ratio of the amplitude for two successive cycles, thus:

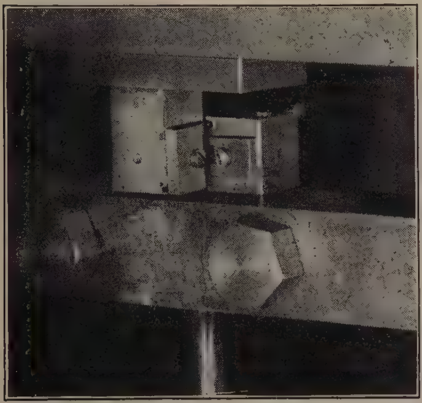
FIG 2a.—DETAIL OF PIVOT SYSTEM.

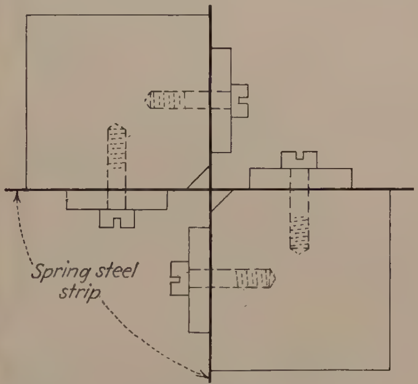

FIG. 2b.—SCHEMATIC DRAWING OF PIVOT SYSTEM.

$$\text{log decrement} = \ln \frac{A_1}{A_0}$$

Another method of expression is the use of the specific damping capacity, which is the ratio of the loss of energy per cycle to the maximum energy of that cycle, or:

$$\text{Spec. damp. cap.} = \frac{W_0 - W_1}{W_0} = \frac{\Delta W}{W}$$

where W_0 is the potential energy of the specimen at the maximum amplitude of the cycle and W_1 that of the next cycle.

Since the energy necessary to twist the bar is proportional to the square of the amplitude, it can be shown that, to a first approximation:

$$\frac{\Delta W}{W} = \frac{\Delta A^2}{A^2} = \frac{2A\Delta A}{A^2} = 2\frac{\Delta A}{A}$$

where A is the amplitude.

Obviously the change in amplitude for a single cycle could not be measured directly from the record and, since the decrement was not independent of the amplitude, an indirect method of calculation was employed. The curve of amplitude versus the number of cycles was plotted on a large scale from a considerable number of measurements taken from the record. Then, at the particular amplitude desired, a tangent was drawn to this curve, the slope of which gave the change in amplitude per cycle. This quantity divided by the amplitude and multiplied by two gave the specific damping. The amplitude was then converted to the maximum fiber stress and the curves of damping vs. stress were drawn. The variation in the results obtained in this way by several independent observers was of the order of 2 per cent. It is believed that the results are reproducible for materials from the same source to within 5 per cent for the low-damping alloys.

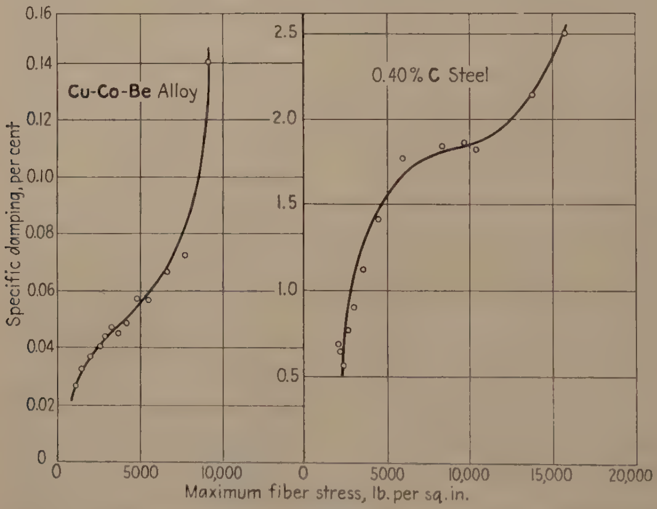

FIG. 3.—TYPICAL CURVES SHOWING RELATION OF SPECIFIC DAMPING CAPACITY AND STRESS.

The Cu-Co-Be sample contains 2.6 per cent Co and 0.4 per cent Be. It was given a solution treatment at 900° C., quenched and aged for 4 hr. at 500° C. The steel sample contained 0.40 per cent C. and was normalized from 850° C. followed by a draw at 650° C.

In Fig. 3 are shown the typical damping-stress curves for a low-carbon steel and for a copper-cobalt-beryllium alloy. It is interesting to see that the damping values in steel are somewhat lower than those found by Brophy[5] using a similar method and by Canfield[6] employing a different method.

CHANGES IN DAMPING CAPACITY DURING AGE-HARDENING

To test the suitability of this apparatus as a metallurgical tool, some observations were made on the changes in damping capacity during the progress of age-hardening of some copper alloys. Two alloys supplied through the kindness of the American Brass Co. had the following analyses:

Alloy A	Per Cent	Alloy B	Per Cent
Cu	97.54	Cu	99.17
Be	2.12	Cr	0.81
Fe	0.30	Si	0.02
Ni	0.30		

These samples were ¼ in. in diameter and 5 in. long for the reduced section with one-half diameter end sections. They were tested in the quenched condition and after various aging treatments. The specific

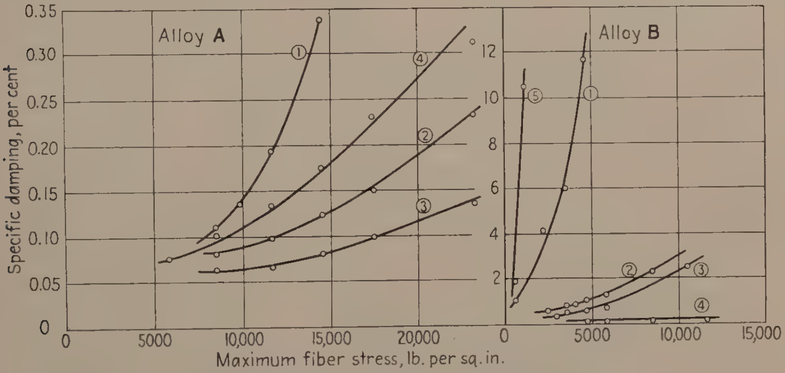

FIG. 4.—SPECIFIC DAMPING CAPACITY VS. STRESS FOR ALLOYS A AND B. Curves correspond to samples in the following conditions:

ALLOY A
(SOLUTION HEAT-TREATMENT AT 800° C.)
Curve 1. As quenched
Curve 2. Aged 30 sec. at 275° C.
Curve 3. Aged 30 min. at 275° C.
Curve 4. Aged 2 hr. at 300° C.

ALLOY B
(SOLUTION HEAT-TREATMENT AT 1025° C.)
Curve 1. As quenched
Curve 2. Aged 20 min. at 500° C.
Curve 3. Aged 30 min. at 500° C.
Curve 4. Aged 2 hr. at 500° C.
Curve 5. Quenched and slight cold work.

treatments are shown on the curves of Fig. 4. Fig. 5 shows the relation of the changes in damping as compared with the hardness changes.

These results are interesting, although far too limited to permit any general conclusions about the behavior of age-hardening alloys. It is plain, however, that the improvement in mechanical properties due to aging is accompanied by a very marked decrease in the mechanical hysteresis and that this is particularly pronounced at the early stages.

The results also show that the changes in damping are of a magnitude that can be measured easily by this method at fairly large stresses; that is, stresses that are appreciable fractions of the elastic limit or yield strength of the alloys. There is considerable question as to whether the damping of a material in several states with widely varying yield strengths should be compared at equal stresses or possibly at stresses corresponding to equal fractions of their yield strengths. Much further work is needed on many of these phases of the problem. The investigation is being continued and will be reported later.

Observations on Design of Torsion Pendulum Apparatus

As the result of more than a year's work with the apparatus described above, certain developments that would improve and simplify the operation of this equipment have become obvious. The optical recording system measures the absolute motion of the inertia bar rather than its relative motion with respect to frame. The ratio of the moments of inertia of the bar and the frame is about one to ten, so that the neutral point or node is slightly above the lower end of the specimen. This makes the stresses, as measured from the record, somewhat in error. Furthermore, the motions of the whole vibrating unit about its wire suspension never can be eliminated completely before starting a run and on the record these motions are superimposed upon the vibrations of the inertia bar. It would be highly desirable to make the frame of the instrument of such a very large moment of inertia that it could be considered as fixed and the recording drum mounted directly on the frame. This large mass could be suspended on wires or even fixed to a solid base. Föppl states[1] that such a procedure causes a considerable loss of energy, but this does not seem to be necessarily so if proper design is employed.

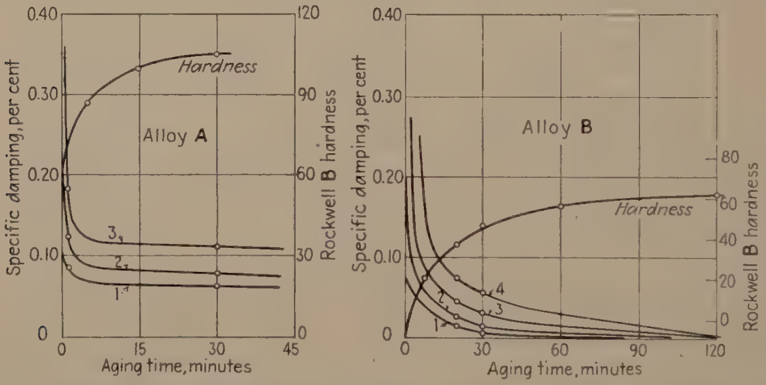

FIG. 5.—CHANGE IN SPECIFIC DAMPING DURING AGING, AT SEVERAL STRESS LEVELS. CHANGE IN ROCKWELL B HARDNESS SHOWN FOR COMPARISON.

Stress levels, in pounds per square inch in outer fiber, are:

Alloy A	Alloy B
Curve 1. 10,000	Curve 1. 2,500
Curve 2. 15,000	Curve 2. 5,000
Curve 3. 20,000	Curve 3. 7,500
	Curve 4. 10,000

If one desires to use some sort of amplitude measurement indicating the relative motion of the two ends of the specimen and independent of the motion of the vibrating unit as a whole, he can spend many hours developing schemes for this purpose. They can take the form of electromagnetic, electrostatic or photoelectric devices, but usually they come out with something like an oscillograph in which a moving mirror makes a record on a drum. It seems far simpler to attach this mirror directly to the inertia bar and eliminate all intermediate steps.

There are two methods of starting the bar oscillating at an amplitude corresponding to the desired stress when the apparatus is freely suspended. One consists of twisting the bar against the energized magnets, bringing the whole apparatus to rest and then releasing; the other involves the use of a source of power at the resonant frequency that, when applied to the magnets, will start the bar oscillating. When the desired amplitude is reached, the power is cut off and the normal decrement curve is obtained. The latter permits a rough check on the damping measurements by a measurement of the power input for constant amplitude. In many ways it is a more flexible method of starting the apparatus and should be included in the construction of new equipment.

The solid specimens do not give a uniform stress over the cross section when deformed in torsion. It is possible that the relation between damping and stress would be more characteristic if hollow cylindrical specimens with fairly thin walls were used. Proper filleting where the reduced section joins the ends is important. Square ends are more satisfactory than cylindrical ends and all later work was done with such specimens. Heat-treating of the specimens should be done in a fixture, so that they will remain as straight as possible. A slight amount of cold work in straightening may have a considerable influence on the damping.

Conclusions

As a result of the experiments discussed above, it has been confirmed that, in age-hardening alloys at least, the damping capacity is quite sensitive to the structural changes taking place. It has been demonstrated that the energy losses in the torsion pendulum apparatus can be reduced to a point where significant changes can be measured with fair accuracy, certainly sufficient for a great deal of survey work. The method is not satisfactory for work at very small strains, and another type of instrument, probably employing the resonance principle, should be used in this region. With two such methods available, the measurement of damping capacity can take its place with measurements of mechanical properties, electrical resistivity, dilation and lattice parameters in the service of the physical metallurgist.

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DISCUSSION

(G. R. Brophy presiding)

G. R. Brophy,* Bayonne, N. J.—Mr. Flinn and Dr. Norton have been very charitable in pointing out the errors of previous investigations. Those errors are real. The very fact that the damping capacities they measure are lower indicates that they are correct and the previous higher results are wrong.

J. T. Norton.—Considerable time has passed since Mr. Flinn finished this work and it may be interesting to point out some of the developments that have taken place since that time. One of the things that troubled us most in this damping apparatus was the fact that the unit itself was freely suspended and to bring it absolutely to rest was a considerable job. We felt that if the mass of the apparatus as a whole could be made large enough, it would be possible to fasten it down solidly and still keep the losses low. We tried that and found that it would work. The new model is a considerable improvement over previous models. An arrangement similar to the freely suspended unit was employed, a heavy frame welded together at the corners, and that was welded to the end of a very heavy channel section. The whole thing was embedded in a massive block of concrete. Runs made with that apparatus on the same specimens used with the freely suspended apparatus gave identical damping curves, and we feel quite sure that this apparatus will give reliable results. It is very much easier to use and it uses very simple samples.

G. R. Brophy.—What are the results with the new apparatus? Are losses considerably less than they were before?

J. T. Norton.—They are just the same as with the freely suspended apparatus. The curves are identical for the same specimen.

G. R. Brophy.—The trend seems to be toward tying down the apparatus.

J. T. Norton.—That is what most people think, but apparently the friction between the heavy mass and the floor is sufficient to prevent any motion. If there is no motion; there can be no loss of energy. The moment of inertia of the new base as compared with the moment of inertia of the inertia bar is enormous, of course, so that its motion cannot be very large.

A. V. de Forest,† Cambridge, Mass.—There may be a relation between damping capacity and primary creep under constant load. Although he was using specimens of entirely different size, Carson showed some curves last year (at the A.S.T.M. meeting) of creep in precipitation-hardened copper alloys in which the age-hardening progressed and the creep diminished up to a certain figure, which, however, was below the maximum hardness value exactly as in these damping-capacity measurements, and overaging also produced an increased creep under steady load over lengths of time up to the order of a few days. He did not go to times comparable with thousands of hours; but it seems as though the elastic behavior in both cases should be related and that tests on the identical specimen under both vibratory conditions of load and static conditions of load might be carried out profitably. The damping test is so much more rapid than any of the creep tests that we might well use damping tests first before running into extensive time on creep tests. I feel that damping properties or creep properties are important from an engineering point of view as well as from the point of view of investigating metallurgical properties alone because, at least for springs, consideration of creep and of damping has led to a great improvement in the selection of the proper alloy and the proper method of heat-treating that alloy.

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† Associate Professor, Mechanical Engineering, Massachusetts Institute of Technology.

Carson found that the heat-treatment that gave the lowest creep was one in which he used a high temperature for a short time; the theory being that that produced perhaps a different level of internal stress than would be produced for the same hardness with a longer time and a lower temperature.

F. G. TATNALL,* Philadelphia, Pa.—I was associated with Dr. von Heydekampf during the years he was in this country espousing the cause of damping capacity as an important physical property. He always emphasized that the damping tester should be suspended and not allowed to rest solidly on any support. Dr. Norton, with his solidly placed tester, improves on the readings of the suspended apparatus. I should like to ask Dr. Norton to write to Professor Föppl, at the Woehler Institute, and tell him what he has done.

J. T. NORTON.—I was afraid the discussion would end in a question of precision; that is, how closely it could be said that there were no losses; how closely those losses could be measured.

D. K. CRAMPTON,† Waterbury, Conn.—Alloy A (Fig. 4) indicates clearly that overaging causes a marked rise in specific damping over that resulting from what might be termed a normal aging treatment. In Fig. 5, it is noted that the aging time was not carried out to a sufficient degree to clearly establish a peak in the hardness curve. Presumably had tests been carried out to longer periods, an appreciable drop in the hardness curve would have occurred. The maximum for alloy A would apparently be somewhere in the vicinity of 30 min. aging time. The question is raised whether a minimum in the curve of specific damping versus aging time would occur, and whether or not this would coincide precisely with the maximum on the hardness curve?

J. T. NORTON.—I do not think we know the answer to that yet. The work we have done so far has been to try out the machine and see that it will work. We have had no systematic program so far.

O. E. HARDER,‡ Columbus, Ohio.—Inasmuch as considerable work has been done with the less precise instrument and in some tests they have been interested primarily in comparative values, is it likely that the comparative values of different materials and different heat-treatments will be in the same relation with the older instruments and with the newer instrument?

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* Baldwin-Southwark Co.

† Director of Research, Chase Brass & Copper Co.

‡ Assistant Director, Battelle Memorial Institute.

G. R. Brophy.—I should like to defend the older work and the correlations we obtained. I believe those correlations are still valid, even though the actual measurements of internal friction may have been high in error.

R. H. Canfield,* Washington, D. C. (written discussion).—It is a pleasure to see renewed interest in the neglected subject of internal friction, and to realize that it is attracting the attention of well informed and equipped workers like the authors of the present paper.

In welcoming the opportunity to comment on this paper, I do not intend to discuss any of the specific results presented in it, but rather to make some general observations which are the fruit of a rather long and intimate acquaintance with the subject.

Considering that this property has been studied experimentally for over 50 years, it is remarkable how few factual data are available regarding it. Is it really a property of materials—a property in the sense of being independent of size of specimen and other considerations—or is the damping capacity dependent on a combination of factors such as size and shape of specimen? It has long been assumed, or rather hoped, that it is a property in the above sense. However, Zener,[7] in a recent theoretical paper, argues that it is the result of the difference between the adiabatic and isothermal elastic moduli, and that it can be computed from the specific heats at constant pressure and constant volume. On this view, moreover, it is also necessary to know the size, shape, and heat conductivity of a given specimen before the actual damping coefficient can be predicted. There is much to be said for Zener's argument. It certainly agrees qualitatively with the known behavior of certain metals; for instance, it accounts for the low damping capacity of aluminum and many of its alloys. On the other hand, it does not include the effects of actual plastic deformation; and there is evidence that some kind of plastic flow may commence at very low stresses. Perhaps it is the latter type of energy dissipation that is of most interest to metallurgists anyhow.

Another matter that is still unsettled is the dependence of internal friction on frequency, and how it may be dealt with mathematically. One thing that is certain is that it is not "viscosity" and cannot be proportional to strain-velocity. This matter has been settled experimentally by Quimby and by Kimball. Zener's work, already referred to, leads to a neat and satisfactory conclusion on this subject. It predicts that the damping factor should be infinitely small for zero frequency, increasing to a maximum value at a certain frequency that is characteristic of the material, and finally gradually decreasing with increasing frequency, approaching zero asymptotically. So far as I am aware, there is as yet no experimental confirmation of Zener's predictions.

A consideration that cannot be neglected in this connection is the damping effect of the air, since these experiments are seldom made in vacuo. I have some evidence that air damping has a more complex relation to frequency than is generally supposed. However, air damping is a small effect in most cases, unless actual drafts of air play on the apparatus.

Regarding the matter of apparatus, I believe that the instrument that ultimately will be found best has not yet been made or designed. I agree with the present authors that for measuring amplitudes no mechanical tracing device is acceptable. The other available methods are: first, optical ones (either with or without photographic recording); and second, electric or electromagnetic. An example of the latter would be a variable air condenser of which one set of plates would be attached to the pendulum, which would produce thereby variations in an alternating current that could be read on a meter.

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[7] C. Zener: *Phys. Rev.* (Aug. 1, 1937) **52**, 230.

Except for certain special experiments, the use of damped free vibrations, as in the Föppl-Pertz machine, is not desirable. Such a method is apt to conceal features of behavior that may be interesting and important. Instead, a device is needed to indicate the actual mechanical power required to maintain the specimen in a state of steady cyclic stress. I have used such an apparatus in the work that has been reported. (Reference 6 and other papers.) I admit that this apparatus was expensive and required considerable experimental and theoretical study for its use. Among the problems studied by means of this apparatus were: the diffusion of hydrogen into a steel specimen during pickling and its subsequent rejection, the aging of various pure irons following overstrain, the age-hardening of dural, and the transitions produced by strain in austenitic steel.

Loss of energy due to defective gripping and other "apparatus losses" have been blamed for the disparity between the experimental results of various workers. The ends of specimens should be much enlarged where they enter grips. On the other hand, when this detail is well attended to, I have secured perfect gripping with the use of a straight cylindrical end on the specimen, gripping it in a chuck similar to a drill chuck. (By perfect gripping, I mean that the whole decrement was less than 0.0002, which means that the grip loss must have been very much smaller.) In discussing apparatus losses one should remember that the pendulum, specimen and support form a "coupled" mechanical system and have therefore two modes of free vibration and two natural periods. When such a system is suddenly started in vibration, there will be an initial space of time when the vibrations will not be steady—the pendulum may even *increase* its amplitude.

The total energy is divided between the pendulum and the support in proportion to the *squares* of their respective amplitudes. Thus if the pendulum makes swings of 10° while the supporting mass is displaced 1°, the energy associated with the latter is only $\frac{1}{100}$ that of the pendulum. Even if every bit of the motion of the support represents energy lost in friction, it can in the case mentioned above account for a decrement of only $\frac{1}{200}$. However, every part of the apparatus should be as tight and rigid as possible. In particular, the component parts of the pendulum itself must be very tight.

I should like to urge upon all workers in this field that they adopt a standard terminology in presenting their results. The theory, though simple, is unfamiliar to most metallurgists; and if, in addition, the results are expressed in strange and varying terms, few people will derive interest or profit from them. As a beginning, I would urge "Internal Friction" as the proper general term for the phenomenon. As the coefficient of damping, let us stick to "δ," the logarithmic decrement of the amplitude. Finally, as a method of expressing results graphically, and at the risk of overemphasizing my own contribution, let me seriously urge the "friction stress versus elastic stress" diagram as being significant and fairly easy to understand.

R. A. Flinn, Jr. and J. T. Norton (written discussion).—There is still a great deal to be learned about the interpretation of damping results but there is enough evidence to indicate that such measurements will be valuable in studying structural changes in metals. In this work one will be interested less in the absolute value of damping capacity than in the changes that are the result of some treatment. If the losses in the instrument can be reduced to a point where they are small in comparison with the changes it is desired to measure, then surely the results are significant. It is fortunate that we have some materials of very low damping which can be employed to give at least an upper limit to the instrument losses. Undoubtedly, the apparatus will be modified considerably with the passage of time but the basic features seem to be sound and workable.

A Theory of Diffusion in Solids

By John E. Dorn* and Oscar E. Harder,† Member A.I.M.E.

(Atlantic City Meeting, October, 1937)

The phenomenon of diffusion, according to the most prevalent conceptions at the present time, undoubtedly played an important part in the formation and distribution of metals and minerals in the earth's crust. Apparently there is good evidence that in the geological rate of cooling diffusion caused numerous materials to separate into individual masses or into duplex structures.

As is well known, the early steels were made by cementation; that is, by heating wrought ferrous metal in contact with carburizing materials so as to produce a relatively high carbon content on the surface. If the process was continued long enough, the carbon diffused throughout the piece. A more homogeneous product depended upon further heating and forging, so that the carbon diffused to a fairly uniform concentration throughout the metal.

In the modern metallurgical industry, diffusion is the basis for many operations; for example, the production of hard surfaces on steels by carburizing, nitriding, cementing with chromium, silicon, boron and beryllium. Castings or ingots as they solidify do not have homogeneous structures, but these structures are made largely homogeneous by suitable process of heat-treating and the resulting diffusion.

It is in modern physical metallurgy, however, that we become greatly concerned about the mechanism of the phenomenon of diffusion. The rates of diffusion, effect of temperature and time on diffusion, and the relation of diffusion to the many properties of the parent metal and the diffusing metal have become important; also, we are concerned with the diffusion of a single metal into a complex alloy. For example, what is the mechanism whereby carbon and nitrogen travel into steel? What is the effect of alloying elements in the ferrous material on the rates of diffusions? What is the effect of simultaneous diffusion of carbon and nitrogen? How does chromium, beryllium, boron, or the like, diffuse into the steel, and what are the effects of alloying elements in the steel previous to the cementation process? These inquiries are by no means limited

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Manuscript received at the office of the Institute April 22, 1937.

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to the ferrous materials because diffusion plays an important part in nonferrous alloys.

For the purpose of finding out more about the general phenomena of solubility and diffusion, the work that initiated the study reported in this paper was undertaken. An attempt has been made to correlate the information available in metallurgy, and to borrow from other fields of science information that could be applied to explain the phenomenon of diffusion and solubility in the solid state of metals as an aid in planning and conducting experimental research.

The Metallic Bond

The migration of a foreign atomic species in the lattice of a solid is a process that not only has important commercial applications but also a fundamental significance in any complete theory of the solid state. Except for Bloch's electron theory* of metals, no adequate theoretical approach to a comprehensive theory of the metallic state has been developed. This deficiency is not due to lack of interest on the part of physicists and chemists in the fundamental processes involved in forming the metallic bond but rather to the very subtle nature of this bond. It may be hoped, therefore, that the process of diffusion may eventually lead to some simple theory of the metallic state, which may find daily use in common metallurgical practice.

For the present, however, there is need of a simple, understandable theory of diffusion; a theory that may not only be applied qualitatively but quantitatively as well; a theory that emphasizes the significance of the fundamental processes involved in diffusion. If this article initiates more careful experimental scrutiny between diffusion and some of the other properties of metals it will have fulfilled its major intent.

Qualitative Sketch of Process of Diffusion†

As R. F. Mehl pointed out in his comprehensive review on diffusion in metals,[11] there are at least three modes of diffusion. Foreign atoms may migrate on the surface of metals, they may migrate in the grain boundaries, and they may migrate within the grain. Only the last of these types will be considered in this paper. Diffusion in this limited sense, therefore, constitutes the transport of atoms from regions of high concentration in the metal lattice to regions of lower concentration.

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* J. C. Slater[14] has discussed the Electronic Structure of Metals from the point of view of Bloch's theory and its recent modifications and improvements. In addition, a comprehensive treatise by N. F. Mott and H. Jones[12] gives the physicist's concept of the metallic state on the basis of quantum mechanics. The specialized mathematical technique required, however, causes the theory to appear inadequate from the practical metallurgist's point of view. Some physicists may contend that no simple picture of the metallic state is possible. The authors prefer to admit the possibility of some yet unknown simplified picture.

† References to previous theoretical discussions on diffusion may be found in Mehl's review.[11] The authors believe the present paper indicates some of the relationships between diffusion and other properties of metals on the basis of a very simple model. Some features of this model, however, are common to those included in the earlier theories.

Before entering into a discussion of diffusion itself, it is advisable to recall certain fundamental facts concerning the architecture of a crystal lattice. The ideal lattice consists of a three-dimensional ordered array of atoms, each of which is bound to all of the others by forces, the nature of which in metals is not completely known. Consequently, each atom within the lattice is held in position by forces that are identical with those acting upon all other identical atoms. The atoms, however, are not fixed rigidly to their sites, but, owing to thermal effects, oscillate about these mean positions. Moreover, these oscillations are not random but synchronous, since each atom is bound to its neighbors. In consequence, a spectrum of three-dimensional elastic vibrations ensues. The frequencies of the modes of vibrations are limited by the boundary conditions just as the allowed frequencies of standing waves in a vibrating string are simple multiples of a fundamental frequency. The frequencies in a solid, however, must be further limited as to the maximum frequency allowed because the energy partitioned to any one frequency cannot be greater than the total energy. By properly weighting the possible frequencies, there results an average frequency, which is called the characteristic frequency. This is the essence of the Debye[6] theory of specific heats of solids, which has been extended by Born and Karman,[3] and more recently by Blackman.

In any real lattice, however, the synchronous motion of the elastic spectrum is seriously modified by secondary effects such as the partial rupture of the bond between two adjacent atoms. This process may most easily be studied by considering the static lattice. In a sense this is equivalent to freezing the elastic lattice in its mean position. The conclusions that follow, therefore, have little individual significance, yet when they are averaged over a great number of individual processes a valid result is obtained.

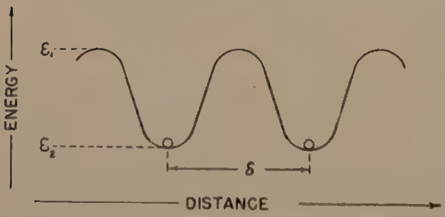

FIG. 1.—POTENTIAL ENERGY WELL.

As mentioned before, each atom is fixed on its proper site with a definite force which is the same for all other identical atoms. In other words, all atoms occupy positions at the bottom of a potential energy well (Fig. 1). Generally the kinetic energy of an atom is much less than $\epsilon_1 - \epsilon_2$, the potential energy of the well. Under these conditions the phase path of the atom is merely oscillating along the lower recess of potential-energy curve drawn in Fig. 1. Oscillations of this type are for the greater part incorporated in the elastic spectrum. Occasionally, however, an atom acquires a kinetic energy equal to or greater than $\epsilon_1 - \epsilon_2$. This atom is said to be loosened from its atomic position; its bond is partially broken and it no longer constitutes an integral part of the elastic spectrum. This loosening is of prime importance in diffusion; in fact, it is the process that makes diffusion possible within the lattice. A liquid metal is completely loosened. It is to be expected, therefore, that the probability of loosening an atom increases as the melting point is approached.

Although the probability of loosening an atom increases with increasing temperature, the time required for an atom to leave its position once it has received sufficient kinetic energy is practically independent of the temperature. Each atom has its maximum velocity at the bottom of the potential energy well. As it approaches the upper walls the velocity rapidly decreases and, if the atom is not loosened, becomes zero. If the atom is loosened, however, it jumps out of its well at the end of its last oscillation. Fortunately the frequency of the oscillation is, on the basis of a simple picture of this process, practically independent of the amplitude of the vibration, depending only upon the restoring forces. Furthermore, these forces remain unaltered if the lattice, the lattice constant, and the atomic species are maintained invariant. Of course, the lattice constant does change with temperature but in this simple theory the slight change that occurs does not sufficiently modify the forces to require the necessity of making a higher approximation.

On the basis of this explanation, it may be believed that the frequency of an atomic jump, once an atom has acquired sufficient kinetic energy to become loosened, is equal to the normal frequency of the atom in the lattice. This, however, is not true in general. Because of steric effects, atoms that have sufficient kinetic energy to become loosened may not be loosened. As they approach the upper walls of the potential energy well they may collide with a neighboring atom and thus rebound into their well. Thus only after a certain number of attempts at loosening will loosening occur. This factor, however, is steric and practically independent of temperature. Hence the time required for loosening depends both upon the period of the atomic oscillation and upon the geometry and size of the atom and its neighbors, and remains practically independent of the temperature.

Up to the present only pure ideal crystals have been considered. Under these circumstances only self-diffusion can take place. Since self-diffusion is a special case of a more general type of diffusion, this subject will be discussed in a subsequent analysis of the general case.

As Mehl[11] has illustrated, in order to have diffusion within the grain the diffusing atoms must form a solid solution. In other words, if one atomic species is completely insoluble in a second, diffusion of the first within the lattice of the second cannot occur. Since there are two types of solid solution, there are two corresponding types of diffusion. The interstitial type is the simpler and for this reason will be considered first.

In a lattice there are vacant spaces that may be filled by foreign atoms provided the foreign atom is small enough to fit into the space available. Such a solid solution is formed by carbon in gamma iron, in which the carbon atom assumes a position at the center of the body of the face-centered cubic lattice of iron. This position will be called an interstitial atomic site. The forces holding the foreign atom in its interstitial site will depend not only on the type of lattice and the lattice constant but also on the electronic nature of the atom forming the lattice and the nature of the atom in the interstitial site. For a given lattice and lattice constant both the shape and depth of the potential well changes when one species of foreign atoms is exchanged for another.

The most effective forces acting upon the foreign atom arise from interactions with its immediate neighbors, and atoms more than a few unit cells away play a rather minor role as far as greatly altering the shape of the potential well is concerned. Therefore, it will be anticipated that small changes in the atomic concentration of the interstitial foreign atom will not greatly alter the probability of loosening this atom. This conclusion is in agreement with the statement that the diffusion constant is independent of the concentration, a fact that is often observed in experiments on diffusion. This is not always true for substitutional diffusion.

The limit of solubility of solid solutions has been studied to a considerable extent by Hume-Rothery.[10] One of the many factors that he found to be influencing the saturation solubility in alloys was the stability of the intermediate phase. For example, the solubility of carbon in gamma iron depends not only upon the stability of the solid solution but also upon the stability of cementite. At equilibrium (i.e., when a saturated solid solution is formed) both phases are equally stable. Under these conditions both phases exist simultaneously and therefore carbon is loosened equally in both phases; the transfer of carbon between the phases is equal in either direction. If, however, the potential energy well for carbon in gamma iron could be made deeper a greater amount of carbon in solution would be required to establish dynamic equilibrium between the two phases. Therefore, for a given intermediate phase the limit of solid solubility increases with the depth of the solid solution potential energy well. Diffusion, on the other hand, decreases as the depth of potential energy well increases. It may be anticipated, therefore, that diffusibility increases with decreasing solubility. This trend has been observed experimentally. Except for this general trend, however, no precise relationship is expected, for, as Hume-Rothery pointed out, other factors, some of which are entirely steric and apparently totally divorced from energy considerations, influence the solubility of primary solid solutions. Furthermore, the solubility depends not only upon the depth of the well in the primary solid solution but also on the depth of the well in the intermediate phase.

The requirement of loosening is necessary for diffusion but it is not sufficient; a concentration gradient is necessary. All atoms of one kind are loosened with equal probability. If, however, all of the possible sites in a plane are filled, no diffusion to this plane can occur. The probability of diffusion to a given plane therefore depends upon the fraction of unfilled sites available; the greater this fraction, the greater the actual diffusion to this plane. It is very likely that atoms jump to the nearest vacant site, therefore jumps between planes that are not adjacent are considered rare. Consequently a plane receives atoms to fill its interstitial sites essentially from its two nearest parallel planes. The plane that has a greater concentration of diffusing atoms will then contribute to the plane having the lower concentration. Thus, diffusion occurs in the direction of the concentration gradient.

In anisotropic crystals, however, the potential well may be lower in one direction than in another, and diffusion will occur most rapidly in the direction in which the energy of loosening is a minimum.

In substitutional diffusion much that has been said for interstitial diffusion is valid. Some points, however, require special attention. A substitutional solid solution is one in which some of the atoms of the original lattice have been replaced by a new species. In general, the positions of the foreign atoms are random throughout the entire lattice. In a perfect lattice, no holes—i.e., no unoccupied substitutional sites—exist. In this discussion only such perfect lattices will be considered. In other words, the effect of unoccupied substitutional sites will be neglected. This idealization is deemed valid because the final equations of the quantitative theory can be shown to be usable even for real crystals. This theory, therefore, may be considered analogous to the ideal gas theory, which is very useful even though no ideal gas exists. If any deviation from the ideal theory occurs, however, it will then be considered opportune to investigate the cause of this deviation. An example of this use will be given shortly.

Since it has been assumed that no unoccupied substitutional sites appear, it is necessary to loosen two atoms before diffusion can occur; one of these must be of the original lattice species and the second of the foreign species. For if one of the original species exchanges places with a neighboring atom of the same species a type of self-diffusion occurs and no resultant change takes place, and if two adjacent atoms of the foreign species exchange places no resultant change occurs.

In this mechanism two potential wells must be considered, one of which originally holds an atom of the original lattice, the other of which holds the solute atom. The depth and shape of the well holding the solvent atom, however, is no longer the same as it was in the pure metal. One of the original bonds has been destroyed and replaced by a bond to the solute atom. If the melting point of the solid solution is lower than that of the pure metal, the original bond has been replaced by a weaker one. The new bond, however, can never be zero, for in these circumstances the solute atom would fall out of the lattice. Hence if C is the coordination number, the number of nearest atoms symmetrically surrounding each atom of the lattice, the depth of the potential well for the solvent atoms never diminishes by more than $1/C$ in dilute solid solutions. Since most solid solutions have lower melting points than the pure metals, the potential energy wells are generally shallower in this case. Under these conditions diffusion of a foreign species is more rapid than self-diffusion. This is an experimental fact. Furthermore, since it is necessary to loosen two atoms in order to promote substitutional diffusion and only one atom for interstitial diffusion, interstitial diffusion is generally more rapid than substitutional diffusion provided no great difference exists in the depth of the potential energy wells.

As soon as two adjacent atoms have sufficient kinetic energy to become loosened, exchange may occur. The time required for this exchange depends upon the period of the oscillations and the geometry of the lattice in the vicinity of the exchanging atoms. In a first approximation, these factors are independent of the temperature. Because of the complications that arise in any attempt to calculate this time from more fundamental quantities, it was considered advisable in this simple presentation to merely show, in the following mathematical treatment, how this time may be determined from experiments on diffusion. In the qualitative treatment it will be sufficient to point out that the time of exchange is essentially independent of the temperature and that it is not merely some average value of the periods of the exchanging atoms but in addition is highly dependent upon the geometry of the process.

As the concentration of the foreign atomic species increases, not one but two or more foreign atoms may be placed adjacent to one of the original species. This, in general, will produce a further reduction in the depth of the potential well of the original atom in addition to changes in the potential wells of the foreign species. When this occurs diffusion becomes a function of the concentration and the simple solution of Fick's law no longer applies. At this point the more general solution, which treats the diffusion constant as a function of the concentration, must be used.

Not all deviations from Fick's law, however, are due to this effect. One very pertinent exception may be illustrated. G. Grube[8] attempted to calculate the diffusion constant for aluminum in alpha iron. In compiling his experimental data by graphically plotting the concentration of aluminum, vertical, versus the depth of case, horizontal, he noted an anomalous flattening out of the experimental curve, after which a more or less anticipated decrease in concentration again took place, with increasing depth of the case. This flattening was observed to occur at a concentration of about 9 per cent aluminum at the lower temperatures employed but for higher temperatures no such flattening was encountered until a concentration of about 12 per cent was reached. The most reliable phase diagrams of this system will show that no change in phase occurs at these concentrations and temperatures. Furthermore, if the energy of loosening were being modified by the increasing concentration of the foreign species, aluminum, the effect should have been gradual. Since this excellent experimental work of Grube's was published, Bradley and Jay[1,2] very thoroughly and carefully investigated the iron-rich portion of the iron-aluminum phase diagram by means of X-rays. They found that up to about 9 per cent aluminum, at the lower temperatures, aluminum takes random positions in the iron lattice. For higher temperatures this occurs up to about 12 per cent aluminum. If the concentration of aluminum becomes greater than this amount, the aluminum atoms begin to take special positions in the iron lattice and initiate the formation of a superlattice. This is accompanied by a decrease in the lattice constant. The observed change in the diffusion constant is thus explained as a consequence of the formation of a superlattice.

Before leaving this part of the treatment it may be advisable to clarify certain points. The theory of diffusion herein presented was designed to apply to diffusion in an ideal lattice. Only in so far as the processes of diffusion in the grain boundary and on the surfaces and edges of a crystal are analogous to lattice diffusion are the statements made expected to apply to these cases also. Considerations of the formation of a new phase during diffusion was completely omitted. It may be pointed out, however, that the formation of a new phase is generally accompanied by recrystallization at its outer boundary and the resulting formation of columnar grains in the direction of diffusion as a result of this recrystallization. Once, however, the new phase is completely formed the laws of diffusion discussed in the previous sections are expected to apply to its individual grains. Moreover, if the grain boundaries are of such a nature that they contain no agent that inhibits migration of atoms within this space, the diffusion along the boundaries is expected to be greater than that in the lattice due to the looser structure in this region. This is the usual experimental observation. If the grains are large or if the boundaries are of such a nature that the enhanced diffusion along them is minimized, the laws mentioned above are expected to apply to diffusion in massive metal. In such cases, however, reasonable precaution must be taken in the interpretation of the experimental results.

Diffusion is usually initiated by placing a thin layer of one metal in intimate contact with another. It has been the opinion of some metallurgists that the former lattice of the diffusing metal may influence its diffusion constant in the new metal. The electronic structure of an atom determines, in part, the depth of its potential energy well and therefore its diffusion in another metal. Since the electronic structure of an atom determines its lattice type, an indirect relationship may exist between the lattice type and the rate of diffusion of an atom. The reaction at the metal surface does not enter into this theory. For solids this has been studied by Jean Cichocki[5] and the readers are referred to his explanation of the process. For gases, however, the chemical reaction occurring at the metal surface has been studied in considerable detail by W. R. Ham[9] in a series of unique experiments on the diffusion of hydrogen in metals. In addition, Dr. Ham has proposed what appears to be an acceptable theory of this process.

DUSHMAN-LANGMUIR EQUATION FOR DIFFUSION

As early as 1922, Dushman and Langmuir presented an equation for application to diffusion in solids. Although the steps of the theory included in its publication were brief, a much more detailed process of the mechanisms had been analyzed. Unfortunately, this was never published. On the basis of the Dushman-Langmuir[7] theory, it is assumed that the probability that an atom will jump from one atomic plane to a second is precisely analogous to the probability for a unimolecular chemical reaction to occur. The resulting equation becomes

$$D = K\delta^2 = \frac{E}{Nh}\delta^2 e^{-\frac{E}{RT}}, \qquad [1]$$

in which D = diffusion constant,
K = the probability an atom will jump,
δ = the jump distance,
E = the energy of activation per mole,
N = Avogadro's number,
h = Planck's constant,
e = the base of natural logarithms,
R = the gas constant, and
T = the absolute temperature.

This equation may be simplified by letting

$$A = \frac{E\delta^2}{Nh} \qquad [2]$$

whence
$$D = Ae^{-\frac{E}{RT}} \qquad [3]$$

In this form numerous experimental tests of the equation have demonstrated its validity and usefulness. There exists, however, reasonable doubt as to whether A can be determined from values of E, δ, N and h, as given in equation 2. Nevertheless, the experimental accuracy of equation 3 has remained intact. Any theory of diffusion, therefore, must result in an equation that has formal similarity to 3. It will be shown that this is true for the theory of diffusion presented in a qualitative fashion in the preceding section.

Probability of Loosening an Atom from Its Lattice Site

The theoretical determination of the probability of loosening an atom from its lattice site is the most important and most subtle problem involved in developing a theory of diffusion for solids. The difficulty that is encountered is associated with the existing lack of knowledge concerning the nature of the metallic bond. The point of view proposed by the authors, however, is indicative of the utility a study of diffusion will have on elucidating the nature of the chemical bond in solid metals.

Since, at present, no adequate simple picture of the metallic bond exists, it is necessary to select, *a priori*, a definite picture and test its validity by comparison in the final form with the experimental equation 3. If a good check is obtained by only one of a great number of selections, reasonable assurance that the single selection is not only a legitimate one but a reasonably accurate one may be entertained. It is hoped that in this way poorer pictures of the nature of metals may be discarded for better and more accurate ones, which eventually may find daily metallurgical usage. It is in this sense that the authors continue this discussion.

Since an attempt is being made to study the metallic bond, it would appear advisable to apply the newer quantum statistical mechanics. At present, however, this is scarcely justified. The accuracy of the experimental technique now being applied would not permit a differentiation between the results of various statistical mechanics. Furthermore, the temperatures generally used are so high that no question of degeneracy need be seriously considered. Until lower temperatures and more accurate measurements are made, it is believed that the Boltzmann statistics will prove satisfactory. Of course, these statistics will not yield as intimate a picture of the bond as would the newer statistics.

On the basis of the Boltzmann statistics, the probability that an atom has an energy ϵ is given by

$$dP_\epsilon = \frac{e^{-\frac{\epsilon}{kT}} dq_i \cdot \cdot \cdot dq_n dp_i \cdot \cdot \cdot dp_n}{\oint e^{-\frac{\epsilon}{kT}} dq_i \cdot \cdot \cdot dq_n dp_i \cdot \cdot \cdot dp_n} \qquad [4]$$

where ϵ = the energy in terms of momenta and coordinates,
k = the Boltzmann constant,
T = the absolute temperature,
q_i = the ith coordinate,
p_i = the ith momentum,
$\oint$ = the integral over all coordinates and momenta.

The integration of this equation becomes very difficult unless the energy is expressed in terms of squared quantities. For simplicity, therefore, assume that

$$\epsilon = a_1 q_1^2 + a_2 q_2^2 + a_3 q_3^2 + \frac{1}{2m}(p_1^2 + p_2^2 + p_3^2) \qquad [5]$$

This is equivalent to considering the atom a point mass oscillating as a three-dimensional harmonic oscillator. If the crystal is isometric,

$$a_1 = a_2 = a_3$$

The probability that such an oscillator has an energy at least ϵ_0 (where $\epsilon_0 = \epsilon_1 - \epsilon_2$, the energy of loosening) can be shown to be

$$p_{\epsilon \geq \epsilon_0} = \left[\frac{1}{(\Gamma s)}\left(\frac{\epsilon_0}{kT}\right)^{s-1} + \frac{1}{\Gamma(s-1)}\left(\frac{\epsilon_0}{kT}\right)^{s-2} \cdots + 1\right] e^{-\frac{\epsilon_0}{kT}} \qquad [6]$$

where $\Gamma(s)$ is the gamma function of s and s is one-half the number of squared variables in the energy expression. For the three-dimensional oscillator

$$s = 3$$

Hence:
$$p_{\epsilon \geq \epsilon_0} = \left[\frac{1}{2}\left(\frac{\epsilon_0}{kT}\right)^2 + \frac{\epsilon_0}{kT} + 1\right] e^{-\frac{\epsilon_0}{kT}} \qquad [7]$$

If, however, this equation is employed it will be found that A of equation 3 becomes a function of the temperature. Experimentally, no justification exists for this selection.

Other attempts to study this probability by assuming various energy expressions yield results that would resuire A of equation 3 to be a function of the temperature. Fortunately, a very simple energy expression yields a suitable result. If

$$\epsilon = a_1 q_1^2 + \frac{1}{2m} p_1^2 \qquad [8]$$

there are only two squared variables in the energy term. In this case the atom may be considered a linear harmonic oscillator. Placing $s = 1$ in equation 6,

$$P_{\epsilon \geq \epsilon_0} = e^{-\frac{\epsilon_0}{kT}} \qquad [9]$$

Equation 9 finally yields an equation formally identical with equation 3, in which A is practically independent of the temperature. In view of the method by which this deduction was made, other equations and hence other explanations may be equally valid. Nevertheless, the simplicity of expression 9, its utility, and, most important, the fact that it yields an expression that agrees with experiments, have prompted its adoption by the authors.

INTERSTITIAL DIFFUSION

In order to promote interstitial diffusion, only one atom need be loosened from its lattice site. The probability of loosening an atom is

$$P = e^{-\frac{\epsilon}{kT}} \tag{10}$$

where ϵ will be called the energy of loosening. After the atom is loosened, transport to an unfilled site may occur. Let τ be the average time required for an atom to move from its initial site to its final site after it once has acquired an energy of at least ϵ. Then the probability of a transport per second becomes

$$P_{\text{sec}} = \frac{1}{\tau} e^{-\frac{\epsilon}{kT}} \tag{11}$$

In this expression $1/\tau$ is a frequency that represents an average frequency of transport once sufficient energy for loosening has been acquired. $1/\tau$ must not be confused with the characteristic frequency of the metal lattice, since in it are averaged steric considerations of the transport mechanism.

As previously indicated, both ϵ and τ are functions of the lattice, the lattice constant, the atomic species present, and the concentration of the atomic species.

Now, consider the effect of the concentration gradient upon the diffusion. In order to simplify the problem let

N = the total number of possible vacant atomic sites per unit area of an atomic plane,
n_0 = the number of filled atomic sites per unit area at x,
$n_0 + dn_0$ = the number of filled sites per unit area at $x + \delta$,
n = the number of unfilled atomic sites per unit area at x,
$n + dn$ = the number of unfilled atomic sites per unit area at $x + \delta$,

where δ is the distance to the nearest parallel plane. Obviously

$$n_0 + n = N \tag{12}$$

$$dn_0 + dn = 0 \tag{13}$$

The probability of finding a vacant site in the plane at x is $\frac{n}{N}$ and the probability of finding a vacant site in the plane at $x + \delta$ is $\frac{n + dn}{N}$. The probability of loosening an atom in the plane at x and having such an atom find a vacant site in the plane at $x + \delta$ is the product of the two mutually exclusive probabilities; namely,

$$\left(\frac{n + dn}{N}\right)P_{\text{sec}}$$

Since there are n_0 atoms per unit area in plane x, the number of atoms per unit area leaving plane x and migrating to plane $x + \delta$ per second is

$$n_0\left(\frac{n + dn}{N}\right)P_{\text{sec}}$$

In a like manner, the number of atoms per unit area leaving plane $x + \delta$ and migrating to plane x per second is

$$(n_0 + dn_0)\frac{n}{N}P_{\text{sec}}$$

The net transport across a unit area of a hypothetical plane at $x + \frac{\delta}{2}$ per second is the difference

$$T = -(dn_0)_t P_{\text{sec}} \tag{14}$$

In expression 14 $(dn_0)_t$ is the change in n_0 at a given time per distance δ. To find dn_0 per distance dx, it is necessary to multiply by δ and divide by dx.

Hence

$$T = -\left(\frac{dn_0}{dx}\right)_t \delta P_{\text{sec}} \tag{15}$$

If c = the concentration of atoms per unit volume,

$$\delta c = n_0 \tag{16}$$

or, differentiating,

$$\delta(dc)_t = (dn_0)_t \tag{17}$$

Substituting equation 17 in 15 and rearranging, there results

$$D = T/_{-\left(\frac{dc}{dx}\right)_t} = \delta^2 P_{\text{sec}} \tag{18}$$

which by definition is the diffusion constant.

Substituting for P_{sec} the value given in equation 11,

$$D = T/_{-\left(\frac{dc}{dx}\right)_t} = \frac{\delta^2}{\tau}e^{-\frac{\epsilon}{kT}} \tag{19}$$

Let

$$\frac{\delta^2}{\tau} = A$$

and

$$\frac{\epsilon}{k} = \frac{E}{R}$$

where E = the energy of transport per mole.

$$D = Ae^{-\frac{E}{RT}} \tag{20}$$

which is in exact agreement with the experimentally verified equation 3.

Then
$$\log D = A' + \frac{B}{T} \tag{21}$$
where
$$B = -\frac{E}{R}$$

SUBSTITUTIONAL DIFFUSION

In substitutional alloys at least two atomic types must diffuse, and the diffusion of one is highly dependent upon the diffusion of the others. For the present this discussion will be limited to a consideration of only two atomic types.

Let n_a = the number of atoms of type a per unit area in a plane at x,
n_b = the number of atoms of type b per unit area in a plane at x,
$n_a + dn_a$ = the number of atoms of type a per unit area in a plane at $x + \delta$,
$n_b + dn_b$ = the number of atoms of type b per unit area in a plane at $x = \delta$,

where δ is the distance to the nearest parallel plane. Since an ideal lattice is being considered,

$$\left.\begin{aligned} N &= n_a + n_b \\ 0 &= dn_a + dn_b \end{aligned}\right\} \tag{22}$$

where N is the total number of substitutional sites per unit area of the plane at x.

For each atom of type a that jumps from plane at x to the plane at $x + \delta$, some atom must jump from plane at $x + \delta$ to plane at x. If the atom returning to the plane at x is of type a no net change occurs. A similar statement is true for atoms of type b. It is necessary to consider, therefore, only exchanges of atoms of type a for b or type b for a. Hence, for diffusion, it is necessary to loosen an atom of type a and an atom of type b. The probability of loosening an atom of type a is

$$P_a = e^{-\frac{\epsilon_a}{kT}}$$

and the probability of loosening an atom of type b is

$$P_b = e^{-\frac{\epsilon_b}{kT}}$$

since the bonds holding an atom in position depend upon the atomic type being held in the lattice. The probability of simultaneously loosening an atom of type *a* and an atom of type *b* is

$$P_{ab} = P_a \cdot P_b = e^{-\frac{(\epsilon_a + \epsilon_b)}{kT}} \qquad [23]$$

On the basis of previous discussions the probability of an exchange in one second is

$$P_{sec} = \frac{1}{\tau_{ab}} e^{-\frac{(\epsilon_a + \epsilon_b)}{kT}} = \frac{1}{\tau_{ab}} e^{-\frac{\epsilon_{ab}}{kT}} \qquad [24]$$

where $\epsilon_a + \epsilon_b = \epsilon_{ab}$ and will be designated the energy of exchange, and τ_{ab} will be called the average time of exchange.

The mathematical treatment from this point forward is practically identical with that previously given for interstitial diffusion. For this reason the method will only be outlined. The number of atoms of type *a* leaving a unit area of the plane at x per second and proceeding to the plane at $x + \delta$, associated with atoms of type *b* leaving the plane $x + \delta$ and returning to plane x is

$$n_a \left(\frac{n_b + dn_b}{N} \right) P_{sec}$$

Similarly the number of atoms of type *b* leaving a unit area of the plane at x per second and proceeding to the plane at $x + \delta$, associated with atoms of type *a* leaving the plane at $x + \delta$ and returning to the plane at x is

$$n_b \frac{(n_a + dn_a)}{N} P_{sec}$$

The net transfer of atoms of type *a* across a unit area at $x + \frac{\delta}{2}$ per second is

$$T = \left\{ n_b \frac{(n_a + dn_a)}{N} + n_a \frac{(n_b + dn_b)}{N} \right\} P_{sec}$$

or

$$T = \frac{(-n_b dn_a + n_a dn_b)}{N} P_{sec}$$

Applying relations 22,

$$T = -(dn_a)_t P_{sec}$$

Completing the analysis,

$$D = T/\left(\frac{-dn_a}{dx} \right)_t = \delta^2 P_{sec} \qquad [25]$$

Substituting for P_{sec} its value as given by equation 24, there results

$$D = \frac{\delta^2}{\tau_{ab}} e^{-\frac{\epsilon_{ab}}{kT}} \qquad [26]$$

which again is identical with equation 3 if

$$A = \frac{\delta^2}{\tau_{ab}}$$

and
$$\frac{E}{R} = \frac{\epsilon_{ab}}{k} = \frac{\epsilon_a + \epsilon_b}{k} \qquad [27]$$

Self-diffusion is a special case of substitutional diffusion,

in which
$$\epsilon_a = \epsilon_b$$

and
$$\frac{1}{\tau_{ab}} = \frac{1}{\tau_{bb}}$$

whence
$$D = \frac{\delta^2}{\tau_{bb}} e^{-\frac{2\epsilon_b}{kT}} \qquad [28]$$

EXAMPLES OF THE APPLICATION OF THE THEORY

The values of ϵ_a and ϵ_b in calories per atom or E_a and E_b in calories per mole should give the depth of the potential well. Unfortunately, $E_a + E_b$ is the quantity that is determined experimentally. In certain cases, however, approximate values of E_a and E_b may be determined. In self-diffusion it is possible to measure $2E_b$ from which E_b may be determined. If the alloys formed with lead have lower melting points than lead, it is reasonable to assume that the wells for the lead atoms are no longer as deep as in pure lead. However, if there are C bonds, and only one is broken, the depth of the well can only diminish at most by $1/C$. The error made in assuming that E_b is the depth of the well in face-centered cubic crystals is less than 8.4 per cent. On the basis of these assumptions, Table 1 may be constructed from information given in Mehl's review on diffusion in metals.[10] The second row, which gives the depth of the well, is obtained by subtracting 14,000 cal. per mole from the value of E_{ab}. In all cases except that for lead, this value may be 1200 cal. per mole too low. If the value for gold could definitely be said to be negative,* an impossibility, it would be necessary to assume that gold forms an interstitial solid solution and 13,000 cal. per mole is the energy of transport and not the energy of exchange. No such

TABLE 1.—*Diffusion of Metals in Lead*

Metal	Au	Ag	Cd	Bi	Tl	Sn	Pb
E_{ab}, cal. per mole	13,000	15,200	18,000	18,600	21,000	24,000	28,000
E_b, cal. per mole	(−1000)	1,200	4,000	4,600	7,000	10,000	14,000
Maximum solubility, atomic per cent	0.05	0.12	0.17	0.35	0.79	0.29	100
Atomic radii for $C = 12$, Å	1.44	1.44	1.52	1.82	1.71	1.58	1.75
External electrons	1.3	1.(3)	2	1.(3)(5)	1.3	2.4	2.4

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* See pages 182 and 184.

statement can be made at present, however, because of the doubtful value of E_b for gold. Several other points of interest are apparent:

1. The metals are arranged in the order of decreasing diffusion. It is immediately apparent that the depth of the potential well E increases for decreasing diffusion.

2. As the depth of the well increases the solubility generally increases. The anomalous cases, Bi and Sn, indicate that differences in the atomic radii influence the solubility sufficiently to upset this relationship.

3. Similarity in the electronic structure of the external shell of electrons causes a tighter binding and a deeper well in spite of low solubility and unfavorable correlation of atomic radii as shown by Sn and Pb. This indicates that diffusion is a problem essentially of energetics and that steric hindrance to diffusion is essentially taken care of in employing an average time of exchange in which all such unknowns are included.

In order to give the readers an estimate of the magnitude of some of the quantities involved in this theory, Table 2 was formed from results obtained by Seith and Peretti.[13] The value for δ was taken to be 2.88Å. In this case the solubility shows a greater correlation with the atomic radii than with the sums of the depths of two wells, E_{ab} It will be noted, however, that similarity of the external electron shell is accompanied with a deeper well, slower diffusion and tighter bonding.

TABLE 2.—*Diffusion of Metals in Silver*

Metal	Sn	Sb	Cd	In	Cu	Au	Ag
A, sq. cm. per day	6.75	4.58	4.18	6.3	5.13	9.6	
E_{ab}, cal. per mole	21,400	21,700	22,350	24,400	24,800	26,600	
$A \times 10^5$, sq. cm. per sec.	7.82	5.31	4.84	7.3	5.94	11.1	
$\tau_{ab} = \frac{\delta^2}{A} \times 10^{11}$ sec.	1.06	1.56	1.71	1.14	1.40	0.75	
Maximum solubility, atomic per cent	13	7	48	20	13	100	100
Atomic radii, Å	1.58	1.61	1.52	1.57	1.28	1.44	1.44
External electrons	2(4)	(1)3(5)	2	1.(3)	1.(2)	1.3	1.(3)

In a paper by Bramley, Haywood, Cooper and Watts,[3] the diffusion of nonmetallic elements in austenite was studied. They found that small amounts of nonmetallic elements in solid solution alter the diffusion constant for some elements considerably. In contrast to the indication that metal atoms appear to be essentially bonded only to the nearer neighboring atoms, as brought out by diffusion experiments of metals in metals, this does not appear to be so for nonmetallic elements in metals. The interpretation we place on this very interesting evidence is that the nonmetals influence the depth of the potential wells of atoms a great distance away. In the light of the electrostatic forces acting in this case, as in the case of ionic crystals, this explanation becomes very plausible.

Bramley and his co-workers studied the diffusion of sulphur in gamma iron (0.030 per cent C, 0.080 per cent Mn, 0.018 per cent P, 0.010 per cent S, and trace Si). They stated that an equation identical with equation 21 would not fit their results. This is equivalent to stating that, in this case, s of equation 6 does not equal 1. We attempted to use other values of s but failed to get a perfect fit between theory and the experiment. Upon returning to equation 21, it was found that only one value—that at about 950° C.—was inconsistent with the theory. Probably some error was introduced into Bramley's experiment at this point. We suggest that it may have been due to inaccurate temperature control, resulting in the existence of some residual alpha iron. Graphically solving for A and B gives $A = 4.56$ and $B = 4.32$. Comparison of our calculated results with Bramley's experimental results is made in Table 3. The deviation occurs only in experiment I. The remaining experiments are a tribute to the difficult work being carefully performed by Bramley and his co-workers.

TABLE 3.—*Diffusion of Sulphur in Iron*

Experiment	$1/T \times 10^3$	Log D Experiment	Log D Calculated	Deviation, Per Cent
I	0.818	0.447	0.59	28
II	0.785	0.740	0.74	0
III	0.760	0.845	0.85	0
IV	0.728	1.000	1.00	0
V	0.703	1.114	1.11	0

SUMMARY AND CONCLUSIONS

1. The nucleus of a theory of diffusion is outlined.
2. This theory illustrates some of the relationships between the energy of loosening an atom and the melting point, diffusibility, and the solubility.
3. Equations for interstitial and substitutional diffusion are developed.
4. Examples of the applications of the theory are indicated.

ACKNOWLEDGMENTS

The authors are duly grateful to Dr. H. R. Nelson, Physicist at Battelle Memorial Institute, Columbus, Ohio, for the time and effort he spent in checking this paper and for the suggestions he offered. To Prof. F. H. MacDougall, of the University of Minnesota; Dr. S. Dushman, of the General Electric Company, and Prof. W. P. Davey, of the State College of Pennsylvania, for their suggestions and encouragement on a preliminary draft of the theory, our appreciation is extended.

ADDENDUM

Since this paper was written an article by Robert F. Mehl on Rates of Diffusions in Solid Alloys has appeared in the *Journal of Applied Physics* [(1937) 8, 174–185]. In this article Dr. Mehl has illustrated important observations on diffusion, among them the dependence of the diffusion "constant" upon the concentration. According to our theory the relation should be

$$\frac{d(\log D)}{dc} = -\frac{1}{\tau}\frac{d\tau}{dc} + \frac{2}{\delta}\frac{ds}{dc} - \frac{1}{RT}\frac{dE}{dc}$$

If these factors are found to be simple general functions of the concentration c, an adequate solution of the partial differential equation for diffusion should be obtainable.

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DISCUSSION

(H. H. Lester presiding)

R. HULTGREN,* Cambridge, Mass. (written discussion).—The authors have attacked a very difficult subject in a simple and straightforward manner. Certainly a simplified picture of the process of diffusion is vitally necessary as a guide to research in this subject. Some of the conceptions they present, however, lead to conclusions that appear improbable to me.

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They picture a metallic crystal as a lattice of atoms, each bonded to all its closest neighbors. The internal energy depends on the number and strength of these bonds. An atom in the act of diffusing undergoes a temporary decrease in coordination number, hence some of these bonds are broken. The breaking of these bonds causes the internal energy to rise, forming a potential barrier, or potential energy well. From this the authors conclude that the stronger the bonds, the deeper the potential well and the slower the rate of diffusion.

Examination of the experimental data of Tables 1 and 2 leads them to the surprising conclusion that unlike atoms form much weaker bonds than do like atoms. However, general results of chemistry lead to a fundamental law that the more different the external electron shells of two atoms, the stronger is the attraction between them. Pauling[15] has studied the subject quantitatively for a number of simple chemical compounds. He concludes that the strength of the bond between atom A and atom B is

$$A:B = \tfrac{1}{2}(A:A + B:B) + \Delta$$

where $A:B$, $A:A$, and $B:B$ indicate strengths of respective bonds and Δ is a quantity that is positive and is larger the greater the difference between the elements A and B. If the total number of bonds in the formation of AB from its elements is unchanged, Δ determines the energy of the reaction.

Hume-Rothery[16] finds the same state of affairs in alloy systems. He says: "Generally speaking, the more electronegative the solute element, and the more electropositive the solvent (or vice versa), the greater is the tendency for the formation of stable intermediate compounds."

Unfortunately, direct measurements of heats of reaction between metals do not seem to be available. However, there is another criterion; we are confident that attraction between atoms leads to a decrease of the distance between them. Jette[17] has studied Vegard's law of the additivity of atomic radii in this light, comparing Vegard's law with Raoult's law for liquids. He concludes that negative deviation from Vegard's law corresponds with specific attraction; that is, positive values of Δ. Compounds are never formed unless there is a negative deviation. Westgren and Almin[18] have shown that there is an unusually strong contraction of atomic volume when compounds are formed.

This argument leads to the conclusion that Δ is positive at the left of Tables 1 and 2 and decreases toward the right. In spite of this, could the bonds $A:B$ increase in strength as we go from left to right? Looking at the equation, we see that this could be true only if the strengths of the bonds $B:B$ increased more rapidly than Δ decreased. Fortunately, there are data tabulated by Mott and Jones[19] on the internal energies of the elements. They give, in kilogram-calories per gram-atom: Au, 83; Ag, 64.5; Cd, 28; Bi, 48.5; Tl, 44; Sn, 76; and Pb, 51. For Table 2: Sn, 76; Sb, 49; Cd, 28; Cu, 76; Au, 83; and Ag, 64.5. In neither case is there any trend. Consideration of difference in coordination numbers does not help.

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From this, we must conclude that there is no simple relation between strength of bond and depth of potential well. Going back to our more complex picture of the metallic state, we see that this is not unreasonable. A metal consists of a lattice of positive ions held together by more or less free electrons. It may be permissible to think of each atom bonded momentarily to one or two of its eight or twelve neighbors, the bond moving around rapidly so that on a time average each of the neighbors is held equally strongly. The decrease in coordination number during diffusion is not particularly important here. The potential barrier is due mainly to the disarrangement of the close packing of all the atoms in the region where the diffusion jump is taking place. Anything that causes a disarrangement or "loosening" of the lattice to be already present before the jump starts naturally lowers the potential barrier. Foreign atoms do disturb the regularity of arrangement and so perhaps generally have lower potential barriers than are present in self-diffusion. If the solute atoms differ greatly in size, they should loosen the lattice more. Foreign atoms, according to this picture, should also increase the rate of self-diffusion of the solvent.

The connection between solid solubility and rate of diffusion derived by the authors no longer applies if depth of potential well is not connected with stability. For an increase of potential barrier not only decreases the rate of diffusion of carbon into gamma iron, as mentioned in their example, but also decreases the rate of diffusion outwards, leaving unaltered the dynamic equilibrium.

For some reason, the authors picture diffusion in a substitutional solid solution as taking place by a simple interchange between two atoms. The earlier idea of a cyclic interchange seems much more probable. Thus an atom in position *A* can jump to *B*, pushing the atom there to *C*, which pushes that atom to *D* and the atom at *D* goes to *A*. Study of a crystal model shows that motion around a ring consisting of three or more atoms results in much less distortion than for two atoms to squeeze by each other. In a cyclic interchange, it is necessary to excite only one atom. Thus, the discussion of the relative depths of potential wells E_a and E_b with the obviously incorrect value for the depth of potential well of gold in lead no longer applies.

R. F. MEHL,* Pittsburgh, Pa. (written discussion).—I do not think anybody would deny that the question of diffusion in the solid state is one of the subjects in physical metallurgy that is of great importance practically, as the authors point out. It is also, at the same time, one of those difficult problems scientifically where the data are not very good; and for the few good data we have, the theoretical explanations are poor. So that one should welcome the competent theoretical treatment we have in this paper by Messrs. Dorn and Harder. I will only comment on a few more or less separate items.

It has been said that there are three types of diffusion in metallic aggregates. When one looks into the evidence for grain-boundary diffusion, it is found to be rather conflicting and not very satisfactory. The best evidence is the work of Langmuir, Dushman and others at the General Electric Co. on the diffusion of thorium in tungsten, in which a very decided grain-size effect was shown, the smaller grain material showing the more rapid diffusion of thorium. However, competent critics on the other side of the ocean adduce evidence that thorium does not form solid solution in tungsten, so one is rather at a loss to know what to think about the whole matter.

Careful metallographic work on diffusion in aggregates gives little evidence for grain-boundary diffusion, except in a few isolated cases. It is known, for instance, that the diffusion of hydrogen in iron does not follow grain boundaries; that is, the rate observed is independent of grain size. This is an interstitial solid solution, and probably this would be true for all interstitial solid solutions. Self-diffusion in lead shows no grain-boundary effect, no grain-size effect. The diffusion of copper in aluminum shows some, as seen by a staining effect, but in the interesting alpha solid solutions of copper the evidence, again, is rather difficult to evaluate. Much of it has been drawn from the loss of zinc from alpha brass by vaporization, which is entirely inadmissible evidence, for as zinc is lost from alpha brass, the grain boundaries open by reason of the volume diminution, so what one is observing is not a grain-size effect except in this special sense.

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The matter is metallurgically of considerable importance in this way: It is a general metallurgical observation that rates of reaction in the solid state depend upon grain size. All metallurgists know the effect of the austenite grain size on decomposition of austenite. The question is this—is the effect of grain size one where the mobility of the atom is greater at the grain boundaries by reason of a higher rate of diffusion of the solute there, or is the greater activity at the grain boundary purely a nucleation effect, apart from any simple relationship to a diffusion coefficient? The evidence seems to be that carbon does not diffuse at the grain boundaries of austenite any more rapidly than within the grain, and it thus appears that the effect of the grain boundary in austenite is one of nucleation alone and not of diffusion, though doubtless these two processes are related in some way.

There are other complications in the diffusion field that really require attention from physicists. For instance, Seith, who has done some of the best work available, measured diffusion rates in a series of lead alloys, and Seith and Paretti, in a series of silver alloys, neglecting any consideration of the effect of concentration on the diffusion coefficient. These data refer to diffusion from a 2 atomic per cent alloy into the pure solvent, and thus approximate the diffusion coefficient limiting on the solvent.

The rate of diffusion as a function of concentration can vary tremendously, and recent work by Dr. Rhines indicates that this variation may be great within a relatively narrow concentration range. For instance, the rate of diffusion of silicon, aluminum, tin, zinc, cadmium, and beryllium in the alpha solid solutions of copper indicates that the diffusion coefficient may vary within even a reasonably limited solid solution range by as much as a factor of 10, increasing from copper to the solid solution limit. Metallurgists will immediately see that this is rather important in connection with factors determining rates of precipitation from solid solutions, for evidently a single D value cannot be applied to the whole precipitation period where the concentration of the matrix is continuously changing. Furthermore, it has been found that these D values extrapolate to a single value for pure copper, whatever the solute, which requires explanation.

There is one problem I wish the authors would study. Until very recently it has been said that diffusion in cubic metals, like iron, aluminum, and so on, does not depend upon crystallographic direction. Brick and Phillips, at Yale, showed by approximate measurements of diffusion coefficients in aluminum that the diffusion coefficient does vary markedly with crystallographic direction. I know of no physical theory that will explain this. It is a problem somewhat similar to that of elastic anisotropy in cubic materials.

Jost has published a book recently that ought to be mentioned in this connection, which treats of rates of chemical reaction and of diffusion in the solid state. He treats in considerable detail the *Fehlordnungserscheinungen* (imperfect order) in crystals, according to the theory of Wagner and Schottky. I wonder if the authors are acquainted with this theory and what they think of it. The development of this theory is rather interesting: there is a logical difficulty in explaining exchange in place in substitutional solid solutions—how can an atom move to an adjacent point if there is already another atom at that adjacent point? Langmuir has handled this problem rather cleverly by proposing that four atoms move in a cycle concurrently, thus providing translation. Until very recently, this has seemed to me the most acceptable theory of the mechanism of atom transport. But Smekal proposed that imperfections are necessary to have diffusion in the solid state. There were some logical difficulties about this proposal, for while it might be true that diffusion should take place along an imperfection plane more rapidly than within the block of the imperfection, still there remained the difficulty that at some time the block must be penetrated else homogeneous alloys would never be formed.

The Wagner-Schottky theory boldly assumes that there are other positions for atoms besides the lattice points of fair probability of occurrence, namely interstitial positions, and that atom mobility consists in the movement of atoms into temporary interstitial positions.

One comment on Bramley's work: Bramley diffused carbon into gamma iron by cementation in gases. In attempting to analyze the carbon-penetration curves, he searched formulas for heat flow until he found one the solution for which fitted his curve; this formula, however, is for the flow of heat through a conductor when the heat is liberated in one burst, then stopped. It is clearly evident that the conditions in the experiment are not analogous and that either the equation selected should not have been used or the boundary conditions were not constant throughout the experiment.

E. H. Dix, Jr.,* New Kensington, Pa.—Dr. Mehl has raised a question concerning the rate of diffusion at grain boundaries upon which I think we have a great deal of evidence. Fig. 2 shows a cross section, including the surface, of a commercial product which consists of an alloy core covered with a layer of pure aluminum. Under microscopic examination, the situation is something like this: In the core there are somewhat elongated grains. In the coating the grain boundaries are normal to the surface of the sheet. During the heat-treatment of this product there is a diffusion of the soluble constituents of the core into the pure aluminum, so that if the specimen is suitably etched to show this diffusion, a series of diffusion peaks will be found at the grain boundaries. In other words, diffusion has definitely followed more rapidly along these grain boundaries than it has within the centers of the grains of the pure aluminum.

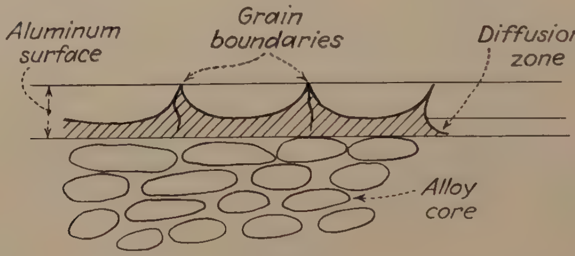

Fig. 2.

W. P. Davey,† State College, Pa.—It seems to me that there has been some unnecessary conservatism in assigning a mechanism to diffusion in metals. Everybody seems to want to think of diffusion as a thing that happens by reason of an atom wandering around in the same way that a small youngster wanders around on a farm if it gets lost. Langmuir, in addition to the theory of the rotating set of four, proposed at one time what seemed to be a much more attractive one, because it really does a few things. He proposed that we imagine diffusion to happen by the motion of the whole planes.

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† Research Professor of Physics and Chemistry, Pennsylvania State College.

Let us assume that we have planes of atoms in a crystal, and that, instead of the heat motion being just a bouncing around of the individual atoms, the heat motion is the shifting up and down or crossways of a whole plane of atoms. In that case the atom of solute can shift along with its plane, and when the plane gets to the end of its oscillation and stops, if some other plane containing that stranger atom happens to move sideways, the atom is carried along nicely. It is not necessary to worry about getting rid of the atom in the place where the new atom is supposed to go to. The difficulty Dr. Mehl brought up is avoided, of having to dispose of the original occupant of the tenement and of having to dispose of the occupant of the second tenement that that original occupant moved into.

This gives a process that goes on with the type of probability postulated by unimolecular reaction, and it is easier to postulate that type of probability for this process than the type of process in which it is necessary to dispose of the locations of three or four atoms at once. In addition to that, this picture of shifting by planes rather than by locations of atoms implies a directional diffusion inside the crystal. It is not an isotropic diffusion, but anisotropic diffusion, which Dr. Mehl would like to have.

The probability of a plane of atoms shifting back and forth as a unit ought to be increased as the population of the plane is increased, and, therefore, as the distance between planes of that sort is increased. That should make it easier for the plane to shift up and down and sideways and in that way there should be a true directional type of diffusion.

Of course, this model is not going to cure all the ills of the world. It will not explain everything in metallurgy, but it does take care of a few things, and I think that this model, or some simple modification of it, is entitled to a little more attention than it has received.

E. U. Condon,* East Pittsburgh, Pa.—The picture Dr. Davey has presented is an interesting one, but I doubt whether it can be held to be valid. I doubt very much whether Dr. Langmuir would insist on that view, although he may have once suggested it.

When one has to consider the rate at which any molecular process occurs, he must remember that the elementary process consists of some means of going from one position of comparative equilibrium to another. The way from the initial state to the period is over a potential energy barrier by the simplest route possible, and at the place where the barrier is lowest. That this is so follows from the fact that the probability that a molecule having a given amount of energy above the average falls off very rapidly with the increase in amount.

The tendency is for the heat motions of the molecules to have a random, chaotic, uncoordinated character. This means that any mechanism that requires the joint cooperative action of a large number of molecules becomes much less probable than a simpler mechanism, even though the energy barrier might be the same in the two cases. In thermodynamic language, the highly organized state is one of low entropy; as entropy always tends to increase, states of low entropy, though they may happen by chance fluctuation from time to time, do not occur as often as they would if their entropy were greater.

The point of view whereby every chemical molecular rate problem is regarded as a quasi-equilibrium between the reactants and an activated complex has been developed greatly in recent years through the work of Prof. Henry Eyring, of Princeton, Prof. M. Polanyi, of Manchester, and Prof. W. Rodebush, of Illinois. Their work should be very stimulating if considered in its relation to the problem of diffusion in metals.

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* Associate Director, Research Laboratories, Westinghouse Electric and Manufacturing Co.

But the main point to be made here is that a mechanism of diffusion, whereby a whole atomic layer of atoms moves at once calls for a tremendous amount of coordination, occurring by chance, in the chaotic motions of individual molecules and for this reason will be very much less probable than a simple atomic interchange in the lattice. I might make a rough analogy in more human terms, because I think this gets at why one must insist on the simplest mechanism possible unless it has to be purchased at too great an energy cost. If we consider the meeting and marriage of human beings, as you know, the rate at which that happens is limited by the question of getting together with the right person, and also by the need of a certain capital to get started with. The capital is related to the energy factor of going over the barrier, but besides that there is a general question of finding the right mate. What I am trying to point out is, how much worse it would be if, instead of there being two sexes, there were, say, a million, and to start a family one had to get a million mates all lined up and organized and selected and found, and then go ahead.

W. P. Davey.—What is the real difference between having a million mates and a million cells in one mate? After all, it just depends on your definition of a mate.

W. P. Condon.—The difference is that one finds the cells already organized before the courting begins.

L. W. McKeehan,* New Haven, Conn.—I was very much pleased by this paper in most of its features. I think, though, there is one point in which the authors became hypnotized by drawing a picture, Fig. 1. In other words, the thing pictured is a potential energy well; but on page 159, the authors say, in regard to the motions of the atoms, that as one approaches the wall of its potential energy well, it may collide with a neighboring atom and thus rebound into its own well. If they had thought a bit more about what constitutes the walls of the well, they would realize that it merely represents the force actions of the neighboring atoms, so that colliding with an atom means that the wall that two atoms approach from opposite directions becomes higher and higher; the chance of their getting over is diminished. Whether that bothers this pussy-wants-a-corner type of diffusion or not, I have not thought out, but it seems to me that it does. That is, in order to get over the boundary so that atom A goes into well B and atom B goes into well A, they will have to execute flanking movements, going through valleys on either side of the hill dividing them.

Of course δ and τ, as the authors point out, must be direction-sensitive in a crystal. That is where the diffusion coefficient's dependence on direction comes in. The value of δ may be guessed from the crystal structure. The probability is that an atom has to get into one of the nearest places, or, at least, into a plane that represents an advance in the desired direction. The value of τ I do not believe can be identified so readily. There must be a great many attempts to get from one cell into another (from one well into another) that are baffled by the cussedness of the wall jumping up in the way.

A. J. Phillips,† Barber, N. J.—I am a little surprised at the impression I gained from Professor McKeehan's remarks, because something over 10 years ago Professor McKeehan very solidly knocked the idea of a solid atom out of my head, and yet he mentions niches and spots that atoms occupy as though they were solid balls in pockets. I am quite certain that he does not mean to convey this impression.

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† Superintendent of Research, Central Research Laboratory, American Smelting and Refining Co.

If we consider that an atom is made up mainly of space, and that we are merely plotting points or average locations, the mechanism of movement of atoms would be easier to understand than if we play with solid balls trying to get one by the other. In other words, the average atomic radius merely defines the field dominated by the atom and does not necessarily mean that another atom cannot pass through that field without completely displacing the first atom. In fact, it is not inconceivable that one atom can pass at least partially through another without impact or destruction of either atom.

W. R. HAM,* State College, Pa.—The authors have mentioned my development of a theory on diffusion of gases through metals, which they say appears to be acceptable. It is not wholly acceptable to me, however. The recent reports I have given have been mostly concerned with the use of gaseous diffusion in the investigation of transitions, particularly in iron and in nickel, but at a meeting a year ago, in discussing the observations of such transitions, by hydrogen diffusion, I mentioned a transition in relatively pure iron, a mild transition that seemed always to be indicated at 850° or thereabouts, and also a similarly faint one at about 940°. These temperatures are now found to be characteristic of hydrogen diffusion through iron, rather than of iron itself.

Of course, there are transitions easily obtained—in the Curie region, at 730° to 770° C. and the 910 α-δ transition, and also a transition that I hope to establish, which is very marked in pure iron at 250° to 300°, ordinarily associated with the A_0 point. That brings up a problem that is stated by inference, at any rate, in the coming *Journal of Chemical Physics* (Nov. 1, 1937). The apparent transition at 850° followed by another one at 950° in iron that is not shown by other data on iron is one of a series.

Furthermore, there is another one at 1000° and so on up; indeed, there is a converging series, indicated by small breaks in the diffusion isobar. Those are certainly characteristic of hydrogen diffusion through iron, for with another apparatus exactly similar in every respect, except that a nickel diffuser is put in place of the iron, no such irregularities are found. This has been checked by different observers. One critic of the paper thought that it was all right except that he did not believe the experimental results were real. I did not believe those results, myself, until I checked them many times, but let us assume for a moment that there is such a series. The series may be represented in a very simple way; that is,

$$T_{\text{Kelvin}} = a\left(\frac{1}{N_0^2} - \frac{1}{N^2}\right)$$

where T is in degrees Kelvin and $N_0 = 3$, $N = 4, 5, 6, 7$, et cetera.

The term value for the 850° break is 6, the next one 7, and so on. The other two terms, in which N is 4 and 5, are masked by the Curie region and the A_0 region. Such a series as this immediately causes one to picture a protonic rotator. It does indicate to me that the iron lattice is essentially ionic in its behavior, so far as hydrogen diffusion is concerned, and possesses a great degree of regularity.

If anybody can give a theoretical explanation of these phenomena that is better than the one I previously suggested, I would greatly appreciate it.

With regard to the discussion of potential barriers, had we not better consider the probability of the hump, itself, varying? It was really suggested by one or two of the previous speakers rather than the probability alone that the thing you are allowing to diffuse may obtain sufficient energy to go over a hump that is regarded as constant.

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* Pennsylvania State College.

J. C. McDonald,* Midland, Mich.—Would more refined experiments on diffusion change the temperature independence of the coefficient of the exponential in the diffusion equation? If so, would the restriction to one dimension of freedom of motion of the atoms be removed?

L. Tonks, Schenectady, N. Y.—The negative value for the heat of diffusion that was attributed to the gold atom in passing through the lead lattice would seem to be somewhat of an anomaly, and should get some particular attention by way of explanation. Another point is the question of the anisotropy of diffusion. Of course, a cubic structure is *per se* not isotropic. After all, the one-one-one direction, the main diagonal, is a very different kind of affair from a one-zero-zero direction, the direction parallel to the cube side.

One might surely expect to find a difference in pheonomena in these two and in other directions. In terms of the detailed picture that was drawn with regard to the energy wells, up the sides of which an atom had to be able to climb in order to interchange its place with another atom, it is easy to see that in the direction of the cube axis, a height of potential barrier different from that reached along the body diagonal or the face diagonal may be reached. There should really be what amounts to a four or five or six—I am not quite certain—dimensional model to completely picture what a migrating atom has to do if it goes in various directions.

R. F. Mehl.—There is a difficulty here concerning anisotropy of diffusion, which may not be evident to everyone. If it is assumed that atoms move along certain directions or planes, it might be expected that anisotropy of diffusion would result, but calculations performed by Dr. McCandless in connection with the rate of growth of oxide films on iron show that such diffusion currents along the various planes (or directions) of the same crystallographic set will average out in calculation, so that the net diffusion for any measured crystallographic direction is the same. The assumption underlying this calculation is that atoms moving along different planes or directions in the same crystallographic family do not mutually interfere; if an anisotropy of diffusion should be found to exist in cubic metals it would have to be concluded that such an interference does occur and that the observed anisotropy is due to that effect.

J. E. Dorn and O. E. Harder (written discussion).—It was not anticipated that this theory of diffusion should be considered the last word on this subject, but merely a highly idealized analysis of the general problem. It is to be expected, therefore, that some of the conclusions drawn may require slight modifications as our experimental knowledge of the subject becomes more exact.

In reply to Mr. Hultgren's remarks, it may be said that the potential energy well is present at all times. Its depth represents the work required to "loosen" an atom. Consequently, a deeper well represents more work, or, in other words, a stronger chemical bond. On the basis of the Boltzman statistics, fewer atoms take part in diffusion for deeper wells and, therefore, less migration occurs for a given concentration gradient.

The authors have not been aware that "general results of chemistry lead to a fundamental law that the more different the external shells of two atoms the stronger is the attraction between them." Two hydrogen atoms form a very stable molecule with an extremely high heat of dissociation in spite of the fact that they have identical structures. There are a great number of molecules composed of hydrogen and dissimilar atoms which have much lower heats of dissociation. Many additional examples may be found which invalidate this law.

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* Research Physicist, Dow Chemical Co.

It was shown in the text that the theory under discussion does not lead to any conclusions contrary to the investigations of Hume-Rothery or others on the stability of intermediate phases. If an intermediate phase is formed, the potential energy well of the solute atom must be shallower in the primary solid solution than in the intermediate phase at the same concentration. This indicates a weaker chemical bond in the primary phase and, correspondingly, a greater diffusivity for a given concentration gradient.

The authors admit that foreign atoms in the lattice may cause a general alteration in the depth of the potential energy well. If the wells become shallower, greater diffusivity results. Some of Bramley's experiments, quoted in the text, indicate that the presence of some nonmetallic substances in iron diminishes diffusivity. The logical conclusion seems to be that these elements cause tighter bonding.

Professor McKeehan's arguments are decidedly in order. It is rather difficult, however, to reproduce a moving potential energy well in a figure. The situation may be clarified if we consider the equipotential surfaces about the atoms in the lattice. Midway between two adjacent atoms is a "pass" of minimum potential energy. If a third neighboring atom is activated sufficiently and is moving in the direction of the "pass," it will surmount it and arrive on the other side. If the third atom is activated to the same extent, but starts traveling directly toward the "peak," occupied by a nucleus, it will rebound. Therefore, some atoms that have enough energy to break through are actually repelled because they started along the wrong path. This was referred to as a collision, which it is. As Professor McKeehan pointed out, during these processes the shape of the potential field changes. All of these directional factors were included in τ. In general these factors are very difficult to evaluate. Dr. Van Liempt, in his excellent work on diffusion, made the simplifying assumption that one-sixth of all the atoms loosened migrate in one of the six possible directions. A number of the ideas incorporated in the present theory are results of Dr. Van Liempt's investigations.

As Dr. Condon pointed out, coordinated motion of a great number of atoms is highly improbable. This suggests that only the simple mechanisms need be considered. Langmuir's theory of cyclic motion involves a coordinated motion of a number of atoms, and therefore is less probable than a reaction involving only two atoms. Cyclic motion with four atoms composing the cycle necessitates that the adjacent atoms are 90° and 180° out of phase. This cannot occur in the normal state of an ideal lattice since neighboring atoms are only slightly out of phase. Perhaps this mechanism is important in diffusion via lattice imperfections. No doubt ideal lattice diffusion, as considered above, and imperfect lattice diffusion, which has been emphasized in Europe, can occur simultaneously. Both appear essential to explain all of the observed facts.

Dr. Phillips' suggestion of ionic migration is interesting and may solve some of the difficulties involved in visualizing the exchange process.

The authors regret that Dr. Ham was led to believe that they would vouch for all of his experimental determinations on the diffusion of hydrogen in metals. They merely stated that his theoretical analysis of the reaction occurring at the metal-gas interface appeared plausible to them.

Dr. McDonald's question is pertinent. In spite of the fact that the temperature dependence of the coefficient for thermionic emission and many chemical reactions has not been determined, it appears that such a determination may be possible for diffusion because of the range of temperatures available and the magnitude of the activation energies. This, however, will require highly refined experimental techniques. Some of the recent work by Dr. Rhines indicates that log D versus $1/T$ does not yield a straight line. It is rather difficult to determine whether this is due to the temperature dependence of the coefficient or to a systematic experimental error.

The obviously incorrect value for the energy of loosening a gold atom, which disturbed Mr. Tonks, may be attributed to experimental error. The E_{ab} value for the diffusion of gold in lead is not known to a high degree of accuracy. Table 1 gives 14,000 cal. per mole for the energy of loosening one lead atom in self-diffusion of lead. Since the solubility of gold in lead is low, it may be assumed that the energy of loosening a gold atom is almost zero. Provided the presence of a small concentration of gold has no effect on the energy required to loosen a lead atom in a gold-lead alloy, the energy for exchange of gold for lead, on the basis of this theory, is only slightly greater than 14,000 cal. per mole. This agrees very well with the experimentally determined value of 13,000 cal. per mole. If coordination is included, a much better value, 12,800 cal. per mole, is obtained. As Dr. Mehl indicated, if the energy of loosening a lead atom were sensitive to small concentrations of gold, this rule could not be applied. This, however, does not destroy the general validity of the mechanism postulated.

A mechanism similar to the one postulated in this paper has been tacitly assumed by Bragg and Williams and also by Bethe in their analyses of long and short range disorder to order reactions. It must be evident to everyone that a unified theory of diffusion, rates of reactions in solids, and disorder to order reactions is highly desirable.

Rates of Diffusion in the Alpha Solid Solutions of Copper

By Frederick N. Rhines* and Robert F. Mehl,† Members A.I.M.E.

(New York Meeting, February, 1938)

It has been shown elsewhere[1] that the data on the rates of diffusion in solid metals are fragmentary and in many cases unacceptable. As a result, relatively little is known concerning the factors determining rates of diffusion and the variations in these rates with temperature.

The first form of Fick's law (equation 1 below),‡ in which the diffusion coefficient D is assumed invariant with composition, has been recognized for many years as only an approximation. The differential equation representing the second form of Fick's law (equation 4 below) has only recently been integrated by Matano,[2] and unfortunately only in cases where a full diffusion-penetration curve (concentration-distance curve) has been obtained can the Matano solution be applied. The proper analysis of diffusion data is thus confined to the data of Grube and Jedele and of Jedele.§ These data are essentially for one temperature alone and do not furnish any information on the variation of the activation heat of diffusion, Q, with concentration: no information exists on the variation of Q with concentration within a single solid solution field.‖

Much of the argument concerning the properties of metals that determine D and Q has been drawn from data in which variations of the quantities with concentration are unknown, for these data have been taken from experiments that could not furnish this information. Speculation concerning the properties of metals that may be effective in determining D and Q on the basis of data in which the chosen D and Q values are averages over wide concentration ranges of values at particular concentrations, ranges often of 100 per cent, is likely not to be fruitful.

Manuscript received at the office of the Institute Dec. 1, 1937.

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[1] References are at the end of the paper.

‡ See mathematical treatment given in ref. 1, pages 12 to 15.

§ Data, G. Grube and A. Jedele;[3] A. Jedele;[4] Analysis of data, C. Matano.[5]

‖ The data given by J. S. Dunn[6] are not those desired, for though Dunn attempted to determine Q for two different compositions in the α Cu-Zn range, his data, obtained by weight losses on vaporization of zinc, are averages for the concentration range between the composition of his initial alloy and copper; furthermore, his technique has inherent disadvantages, as shown later in this paper.

The work of von Hevesy and of Seith* on the rate of diffusion of a long series of elements in lead and in silver, respectively, has furnished most of our conceptions concerning the factors determining rates of diffusion and the temperature coefficients of these rates. These data are limited to rather dilute alloys, usually in the neighborhood of 2 atomic per cent of the solute. In systems in which the degree of solid solubility is high, the data must be considered as applying only to dilute solutions. When the solid solubility is low, the chosen concentration difference of 2 per cent may actually cover much or all of the solid solution range, and thus the data must again be averages over this relatively extended range of concentrations. Data presented below will show that variations in D and Q may be relatively great within a relatively small solid solution concentration range.

The data upon which the Matano method has been used have been obtained from single experiments under one set of experimental conditions, and no effort has been made to see how accurately the results can be reproduced. In view of the lack of precision in diffusion data and of the frequent lack in published papers of a critical attitude toward the experimental procedure and evaluation of data, it seems quite timely to perform a reasonably long series of measurements of D, in which an attempt is made to maintain a highly critical objectiveness. Furthermore, such data, in which the variation of D and Q with concentration is determined, will furnish a more searching test of the Dushman-Langmuir equation than any heretofore available. While this equation is very useful, it seems inadequate in some respects and is in need of further test.[1]

It is likely that a determination of the rates of diffusion in the alpha solid solutions of copper with the metals of the B subgroups should be more useful in studying the factors that determine diffusion rates than similar data on lead alloys, for the former systems have proved particularly susceptible to the discovery of the factors that determine the occurrence of intermediate crystal phases, and those which determine solidus and liquidus temperatures, whereas no success of this sort has been attained for the systems of lead. Although it has been proposed that low solid solubilities, large differences in melting point between solvent and solute, large differences in atomic radii, increasing separation of the solvent and solute in the periodic table, among other minor factors, contribute toward high diffusion coefficients, it has been said that none of these factors is consistently effective except that of the relative position of the solvent and solute in the periodic table.[9] This factor is not easy to define more closely, but its operation in the several properties of the structurally analogous alpha copper solid solutions encourages a study of the rates of diffusion in these systems.

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* Many references: see list given in ref. 1; also W. Seith[7] and W. Seith and E. A. Peretti.[8]

It has long been clear that many changes in phase in the solid state in alloys proceed by the operation of the diffusion process. It will be readily seen that in precipitations from solid solutions, as, for example, in duralumin, the concentration of solute in the decomposing matrix will progressively decrease as the precipitation progresses. Thus, if the rate of diffusion in the solid solution should vary with concentration, the rate of precipitation will vary during its course in some related though undefined manner. It is important to know what variation in D to expect in analyzing the factors that determine the rates of such changes.

It is probably unnecessary to point out the fundamental character of diffusion data. The diffusion coefficient D represents the atomic mobility, and the activation heat of diffusion Q is ordinarily taken as a measure of the potential barrier that surrounds a diffusing atom.[1,10] Although the physics of solid solutions, or even that of solid single metals, is not sufficiently advanced to provide real use for such data, it must find its usefulness in time. Such data may prove of wide importance, for all processes depending on atom mobility, even in the absence of concentration gradients, may well be determined by D and Q values for alloys of particular concentration; such processes as recrystallization, recovery,* and creep are cases in point, and indeed Kanter[11] recently presented a fundamental and successful analysis of minimum creep rates on this basis.

The alloy systems of copper with the elements of the B subgroups include a large number; the systems selected for this study were those for which alloys were readily available or easy to prepare. The systems chosen were: Cu-Zn (in which two base alloys of different compositions were employed), Cu-Al, Cu-Be, Cu-Cd, Cu-Si and Cu-Sn.

EXPERIMENTAL PROCEDURE

In order to determine the rate of diffusion of one metal in another at a specified temperature, it is necessary only to learn the exact distribution of the metals in the zone of interpenetration before and after a definite time interval of diffusion. This was accomplished by analyzing successive layers cut from cylindrical samples which had been made by copper-plating alloy bars and causing interdiffusion to take place between the alloy and the copper at fixed temperatures for predetermined periods of time. The method, though simple in principle, requires such a high degree of experimental precision in a diversity of operations that an adequate basis for judging the reliability of the final results can be given only by presenting a discussion of the details of the procedure.

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* See references to van Liempt in ref. 1.

Seven binary copper-base alloys were made commercially for this work from electrolytic copper and the purest available grades of aluminum, cadmium, silicon, tin, zinc, and beryllium-rich copper. Each composition was chosen within the α range of the system involved near the maximum of the solid solubility, except in Cu-Zn, where an additional concentration near the middle of the α field was selected. The material was received in the form of rolled bars ¾ in. in diameter. These were annealed in order to remove local inhomogeneities as completely as possible; gross segregation along the lengths of the stock bars could not thus be eliminated, and it was necessary, therefore, to obtain an individual analysis for each sample of bar used in a diffusion experiment. After the completion of the diffusion treatments, the center part of the core of each sample was drilled out and analyzed for both copper and the alloying element. The "core analyses" obtained in this way are listed in Table 1, column two. Here the values for the alloying elements only are given. Those for cadmium, silicon, tin and beryllium are from direct analysis, while those for zinc and aluminum are taken from the difference between the copper content and 100 per cent, corresponding to the practice followed in the actual diffusion analyses. Adding the values for copper and the alloying elements, the following total metal contents were accounted for: Cu + Al = 99.18 per cent, Cu + Be = 100.03 per cent, Cu + Cd = 99.90 per cent, Cu + Si = 99.49 per cent, Cu + Sn = 99.85 per cent, Cu + Zn (13) = 99.88 per cent, and Cu + Zn (30) = 98.91 per cent. In the 30 per cent Zn alloy, 0.88 per cent Sn was found; 0.06 per cent Fe and 0.02 per cent Al in the silicon alloy, and 0.05 per cent Fe in the beryllium alloy. No other foreign elements were reported.

After the homogenizing anneal, the samples were turned to a diameter of 0.7 in. in a lathe and were cut into lengths of 3½ to 4 in. In order to obtain uniform reference surfaces, the bars were transferred to a precision lathe, in which they were carefully turned to about 0.65 in. in diameter within an accuracy of ± 0.0003 in. over the entire length of each. The final stage in this process involved very careful grinding with 0000 emery paper, so that the surfaces were of almost reflecting quality. To make the whole of the surfaces of the bars accessible for machining they were turned between centers.

The deposition of the copper plate upon the alloy cores proved to be a matter of more difficulty than was anticipated, because an extraordinarily clean deposit was required to avoid the formation of blisters during the subsequent annealing treatment. It was finally found that minute particles of entrapped greasy material were responsible for the blistering. Their presence could be avoided by cleaning the samples with pumice on a wet cloth immediately before plating. The bars were transferred at once to the plating bath, and care was taken to avoid contamination by finger prints or through the accumulation of any slight oily scum on the surface of the electrolyte. A copper sulphate solution of density 19 Bé., carrying 40 grams per liter of sulphuric acid and a minute quantity of colloidal calcium sulphate, was used at room temperature as the electrolyte. The current density used, about 20 amp. per sq. ft., was not critical, but it was important that there be no interruptions in the power supply. The bars themselves were so mounted that they could be rotated rapidly about their cylinder axes during the entire plating operation. In addition, a canvas diaphragm was placed between the cathodes and anodes and the electrolyte was rapidly circulated. Scrap electrolytic copper was used for anodes. The thickness of the finished plates at the end of four or five days varied between 1½ and 2 mm. Of the various plating techniques employed, this one alone proved successful.

TABLE 1.—*Annealing Temperatures*

Sample No.	Core Analysis (Balance Copper)	Temperature of Diffusion, Deg. C.	Time of Diffusion, Days	Sample No.	Core Analysis (Balance Copper)	Temperature of Diffusion, Deg. C.	Time of Diffusion, Days
	Al, Per Cent			23*	10.24	700	34.46
	(By difference)			24	10.35	753	7.15
1	8.65	700	22.42	25	9.88	751	14.00
2*	8.50	700	38.40	26	10.28	798	9.06
3*	8.53	699	86.96	27	10.17	802	23.56
4	8.50	755	7.13		Zn, Per Cent		
5	8.42	750	14.00		(By difference)		
6	8.32	903	1.08	28	12.89	751	18.98
	Cd, Per Cent			29	12.93	751	37.17
	(Determined)			30*	12.92	840	5.73
7*	1.24	500	83.17	31	13.01	840	11.99
8	1.02	540	12.54	32	12.83	841	23.76
9*	1.07	542	48.67	33	12.88	902	0.83
10	1.09	579	12.45	34	12.96	897	1.31
11	1.08	580	49.63	35	13.02	900	3.02
12*	1.01	580	86.00	36	31.02	750	6.83
	Si, Per Cent			37	31.15	750	13.00
	(Determined)			38*	31.75	840	5.73
13	5.05	700	17.92	39	30.85	840	8.98
14*	5.08	700	37.46	40	30.84	897	1.31
15*	5.08	700	66.96	41	30.63	900	3.02
16	5.04	750	6.83		Be, Per Cent		
17	5.00	747	13.64		(Determined)		
18*	5.06	750	26.97	42*	1.54	701	24.98
19	5.06	798	9.06	43	1.56	799	8.82
20	5.1	802	23.56	44	1.56	801	17.85
	Sn, Per Cent			45	1.49	800	34.71
	(Determined)			46	1.47	851	9.42
21	10.26	700	7.00	47	1.53	850	18.75
22*	10.27	700	14.39				

* Treatment interrupted.

Although relatively smooth and uniform copper deposits were obtained, it was thought best to machine the outer surface of each bar to a uniform diameter. Occasionally the turning centers on the samples were fouled in the course of plating or annealing and had to be relocated.

This was done by polishing and etching the ends of the bar and then centering it in the lathe chuck, using a Brinell microscope mounted on the toolholder to check accurately the location of the alloy-copper interface while the lathe head was slowly rotated.

The diffusion-annealing treatments were carried out in muffle furnaces equipped with automatic temperature controllers. In order to minimize the variation in the heating and cooling cycle, the samples were placed inside heavy copper blocks of high heat capacity made by cutting 10-in. lengths from an oxygen-free high-conductivity wirebar and drilling longitudinal holes of a size just great enough to accommodate the diffusion samples. With this arrangement the temperature variation at the sample over a single heating and cooling cycle was considerably less than 1° C. Over the total annealing periods, the maximum variations observed were ±3° C. In order to prevent oxidation, the chambers containing the diffusion specimens were plugged with tapered copper stoppers and a small amount of charcoal introduced with each sample. Care was taken also to avoid placing two samples of unlike composition in the same chamber at the same time, in order that vapor-phase diffusion should not contaminate the samples.

In Table 1 are listed the annealing times and temperatures. These were chosen in such a way as to yield samples with the largest possible concentration-penetration zones without bringing appreciable quantities of the diffusing element to the outer surfaces of the copper plate. As a guide in establishing the times, a single sample of each alloy was annealed for a series of time intervals at each temperature, and the outer layers of the specimen were periodically examined with the spectroscope for the presence of traces of the diffusing element. The examinations were carried out after each trial annealing interval by first machining a few thousandths of an inch from the copper plate in a band about ¼ in. wide. Upon this cleaned surface the spark was then struck for spectrographic analysis. The precaution of turning off the thin layer from the outside was necessary in order to avoid erroneously high solute concentrations on the surface resulting from vapor-phase contamination from the ends of the samples. At the time of the first appearance of spectrographic traces of the diffusing element the annealing treatments were discontinued and the bar was set aside for chemical analysis. Following this procedure it was found in most cases that chemically (in contrast to spectrographically) detectable quantities of the diffusing element were present from about the middle of the copper plate inward. Having determined a favorable annealing interval in this way, one or two others were chosen by approximately halving or doubling the time. Diffusion-annealing times in excess of three months were avoided.

The series of annealing treatments extended over a period of almost two years, which led to some difficulty in maintaining the furnace equipment in perfect working order. As a result of occasional power failures and other mishaps, certain of the treatments were interrupted for indefinite intervals of time, so that it is impossible to give an accurate figure for the length of the annealing period. The samples so affected are marked with an asterisk in Table 1. In addition, there is an uncertainty of perhaps 0.1 per cent of the annealing time introduced during the periods of heating and cooling. In no case, however, is the uncertainty in the time greater than 1 per cent, and it is generally much less. Since time appears in the diffusion equation as a reciprocal first degree factor, the percentage error in the determination of the diffusion coefficient introduced from this source is very nearly equal to the percentage error in the measurement of the time, and thus in none of the present cases will it be greater than 1 per cent.

The temperature of each furnace was checked and recorded several times each day. From these readings a weighted average of each annealing temperature was taken. This was done by estimating the time at which the furnace was within each one-degree interval of temperature, multiplying by the corresponding temperature, adding, and dividing by the total time. Within the narrow range of temperature variations dealt with, this very approximate method of correction is all that is required. It is safe to say, however, that the values recorded in Table 1 are accurate within ±1° C. It can be shown that an error of 1° C. in measuring the temperature at 500° C. will introduce a maximum error of about 3 per cent in the diffusion coefficient, whereas at 900° C. the effect of an error of 1° C. will be reduced to about 1.5 per cent.

Samples for chemical analysis were taken from each bar by replacing it in a Rivett precision lathe and machining successive layers of a thickness of approximately 0.003 in. A piece ¼ in. long at each end of the cylinder was preserved for metallographic examination. In all, 40 layers were turned from each sample, the diameter after each cut being carefully measured with micrometers. In addition, the samples were so taken that about half of them were in the zone of the original copper plate and the other half immediately opposite in the zone of the original alloy. From each group of 40 samples, 12 were selected for chemical analysis, and the remainder were preserved for future check samples. The selections were made in such a way as to distribute the compositions as evenly as possible along the concentration-penetration curve and to avoid samples where any uncertainty concerning the precision of the cutting operation was suspected.

Although the calculation of the diffusion coefficient requires a knowledge of the distances involved at the temperature of diffusion, no appreciable error is introduced by measuring them at room temperature, for the greatest difference that could have been encountered is less than one-fifth of the value of the limit of sensitivity of dimensional measurement.

The analytical samples were analyzed for their copper contents by the usual electrolytic procedure. The beryllium, cadmium, silicon and tin alloys were analyzed for these elements as well as for copper.

The probable magnitude of the analytical error in determining the compositions of the samples varies from system to system and from the outside to the inside of the diffusion zone. Where the analysis has been made by the difference method, the error may be expected to be greatest at the core, since any impurities in the core alloy will be distributed in the diffusion zone in somewhat the same way as the diffusing element. That is, the impurities will range from nearly zero in the copper plate to a maximum in the core. This condition was found in the beryllium alloys, which were analyzed for iron as well as for beryllium and copper. The recorded values for aluminum determined by difference are doubtless reliable within 0.1 or 0.2 per cent at the core. Zinc was also determined by difference, whence an error ranging from 0.1 per cent at the outside to 10 times as much at the core may be anticipated. Beryllium was determined directly. Cadmium was determined directly in most of the samples; nevertheless some erratic results were obtained, owing to the small weights of the samples and the low percentage of cadmium present, so that an error of 0.2 per cent may exist in some of the figures. Silicon was also determined directly, the low percentages spectroscopically and the high chemically. Although no statement was made by the analyst, it seems reasonable to assume that the values given are correct within 0.02 or 0.03 per cent. The figures for tin by direct analysis are believed to be accurate to 0.03 per cent.

In Table 2, the analytical determinations and the average distance of each sample from the original copper-alloy interface are recorded. The average distance was taken as the radial distance from the center of each analyzed cut to the original interface.

CALCULATION OF THE DIFFUSION COEFFICIENTS

The values recorded in Table 2 are suitable for the plotting of concentration-penetration curves in which concentration is represented as a function of distance from the original interface. The methods by which such curves may be evaluated have been discussed in detail elsewhere.[1]

Grube and Jedele[3] applied Fick's law in its simplest form; namely,

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad [1]$$

This equation assumes that D is invariant with concentration. Under the experimental conditions obtaining here, the solution to this equation (ref. 1, bottom of p 14) is

$$c = \frac{c_0}{2}\left[1 - \phi\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad [2]$$

TABLE 2.—*Experimental Data*

Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c	Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c	Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c
1	0.866	0.10	7	0.8484	nil	13	0.848	0.00
1	0.584	0.00	7	0.5613	nil	13	0.554	0.00
1	0.376	0.00	7	0.3378	nil	13	0.319	0.05
1	0.235	0.29	7	0.1981	0.07	13	0.185	0.93
1	0.161	0.95	7	0.1295	0.21	13	0.114	2.03
1	0.090	2.55	7	0.0686	0.44	13	0.050	2.85
1	0.020	3.93	7	0.0127	0.56	13	−0.009	3.29
1	−0.050	5.20	7	−0.0533	0.59	13	−0.058	3.75
1	−0.116	6.34	7	−0.1143	0.87	13	−0.104	4.08
1	−0.258	7.58	7	−0.2438	0.90	13	−0.216	4.46
1	−0.475	7.96	7	−0.4547	0.99	13	−0.376	4.86
1	−0.687	8.15	7	−0.7722	1.02	13	−0.653	5.30
2	0.789	0.07	8	1.023	0.07	14	0.859	0.00
2	0.519	0.10	8	0.691	0.08	14	0.565	0.00
2	0.325	0.26	8	0.483	0.38	14	0.347	0.15
2	0.185	1.37	8	0.331	0.19	14	0.199	1.45
2	0.112	2.23	8	0.177	0.20	14	0.128	2.25
2	0.051	3.36	8	0.111	0.29	14	0.057	2.77
2	−0.006	4.49	8	0.046	0.31	14	0.003	3.13
2	−0.071	5.30	8	−0.012	0.38	14	−0.039	3.45
2	−0.138	6.01	8	−0.060	0.75	14	−0.081	3.60
2	−0.282	7.26	8	−0.173	1.03	14	−0.179	4.09
2	−0.488	7.84	8	−0.464	0.63	14	−0.303	4.46
2	−0.787	8.29	8	−1.056	1.93	14	−0.606	4.92
3	0.724	0.00	9	0.8230	nil	15	0.810	0.02
3	0.475	0.05	9	0.5283	nil	15	0.527	0.35
3	0.287	0.98	9	0.2972	Trace	15	0.310	1.29
3	0.159	2.95	9	0.1905	Trace	15	0.189	2.29
3	0.097	3.78	9	0.1422	0.17	15	0.112	2.36
3	0.036	4.50	9	0.0800	0.19	15	0.051	2.63
3	−0.033	5.07	9	0.0178	0.39	15	0.001	2.96
3	−0.105	5.80	9	−0.0470	0.79	15	−0.057	3.21
3	−0.174	6.24	9	−0.1118	0.80	15	−0.119	3.46
3	−0.316	7.00	9	−0.2235	1.04	15	−0.237	3.79
3	−0.542	7.62	9	−0.4166	1.00	15	−0.470	4.35
3	−0.842	8.02	9	−0.7341	0.96	15	−0.859	4.94
4	1.178	<0.01	10	1.034	0.07	16	0.792	0.00
4	0.705	0.01	10	0.566	0.07	16	0.507	0.00
4	0.546	<0.01	10	0.345	0.08	16	0.281	0.75
4	0.414	0.01	10	0.1854	0.12	16	0.154	2.13
4	0.316	0.03	10	0.1118	0.13	16	0.091	2.74
4	0.224	0.89	10	0.444	0.43	16	0.029	3.18
4	0.090	3.16	10	−0.0139	0.54	16	−0.020	3.51
4	0.008	5.26	10	−0.117	1.03	16	−0.066	3.72
4	−0.126	6.89	10	−0.236	1.30	16	−0.113	3.91
4	−0.240	7.39	10	−0.4724	0.88	16	−0.290	4.26
			10	−0.6451	0.70	16	−0.493	4.70
			10	−0.8763	0.99	16	−0.777	5.00
5	0.853	0.11	11	0.7391	Trace	17	0.615	<0.01
5	0.546	0.11	11	0.4851	Trace	17	0.462	0.26
5	0.330	0.52	11	0.2769	0.16	17	0.329	0.72
5	0.169	2.33	11	0.1537	0.10	17	0.259	1.36
5	0.112	3.30	11	0.0902	0.20	17	0.186	1.95
5	0.058	4.13	11	0.0267	0.43	17	0.113	2.43
5	−0.005	4.91	11	−0.0356	0.56	17	0.037	2.95
5	−0.071	5.50	11	−0.0978	0.93	17	−0.036	3.34
5	−0.131	5.89	11	−0.1600	1.00	17	−0.183	3.88
5	−0.243	6.70	11	−0.2997	1.16	17	−0.389	4.44
5	−0.446	7.46	11	−0.5740	1.16			
5	−0.725	7.91	11	−0.8915	1.09			
6	0.950	0.01	12	0.759	Trace	18	0.781	0.04
6	0.622	0.00	12	0.436	Trace	18	0.516	0.58
6	0.408	0.00	12	0.197	Trace	18	0.307	1.57
6	0.263	0.87	12	0.081	0.16	18	0.187	2.35
6	0.189	1.91	12	0.041	0.11	18	0.117	2.71
6	0.108	3.19	12	−0.003	0.35	18	0.055	2.94
6	0.032	4.35	12	−0.048	0.56	18	0.004	3.20
6	−0.039	5.08	12	−0.094	0.56	18	−0.047	3.28
6	−0.113	5.48	12	−0.135	0.60	18	−0.100	3.53
6	−0.269	6.59	12	−0.253	0.98	18	−0.197	3.86
6	−0.488	7.51	12	−0.465	1.00	18	−0.386	4.22
6	−0.771	7.82	12	−0.881	1.05	18	−0.671	4.62

TABLE 2.—(*Continued*)

Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c
19	0.988	0.10
19	0.540	0.15
19	0.310	1.88
19	0.196	2.62
19	0.132	2.77
19	0.077	3.18
19	0.010	3.45
19	−0.066	3.74
19	−0.154	3.97
19	−0.331	4.71
19	−0.490	4.97
19	−0.818	5.25
20	0.822	0.10
20	0.535	1.17
20	0.312	2.36
20	0.155	2.94
20	0.095	3.10
20	0.047	3.24
20	−0.004	3.38
20	−0.060	3.53
20	−0.118	3.63
20	−0.240	3.85
20	−0.429	4.12
20	−0.735	4.45
21	1.311	0.00
21	0.928	0.00
21	0.674	0.00
21	0.410	0.00
21	0.264	0.202
21	0.110	2.54
21	0.033	5.11
21	−0.027	6.92
21	−0.108	8.45
21	−0.306	9.71
21	−0.484	9.79
21	−0.817	9.97
22	0.966	0.00
22	0.688	0.00
22	0.399	0.00
22	0.1905	1.37
22	0.128	2.46
22	0.091	3.36
22	0.034	4.96
22	−0.047	6.72
22	−0.136	8.09
22	−0.326	8.67
22	−0.568	9.48
22	−0.839	9.42
23	0.876	0.00
23	0.564	0.067
23	0.367	0.59
23	0.224	2.24
23	0.160	3.33
23	0.095	4.29
23	0.030	5.36
23	−0.029	5.82
23	−0.091	6.45
23	−0.231	7.30
23	−0.419	8.26
23	−0.709	9.27
24	0.784	<0.08
24	0.669	<0.11
24	0.564	0.02
24	0.355	0.66
24	0.253	1.78
24	0.174	3.14
24	0.095	4.58
24	0.018	5.37
24	−0.026	6.46
24	−0.096	7.19
24	−0.175	8.01

Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c
25	0.7341	0.068
25	0.4521	1.03
25	0.2692	2.98
25	0.1473	4.37
25	0.0927	4.83
25	0.0381	6.05
25	−0.0178	6.57
25	−0.0864	7.13
25	−0.1613	7.64
25	−0.3023	8.58
25	−0.5182	9.51
25	−0.8280	10.01
26	0.758	0.10
26	0.561	0.71
26	0.377	2.10
26	0.137	4.85
26	0.069	5.29
26	0.020	5.75
26	−0.023	6.11
26	−0.084	6.54
26	−0.201	7.46
26	−0.410	8.46
26	−0.879	9.44
26	−1.337	9.86
27	0.7264	0.809
27	0.4343	1.712
27	0.2299	2.495
27	0.0927	2.825
27	0.0521	2.916
27	0.0102	2.966
27	−0.0419	3.164
27	−0.1054	3.226
27	−0.1727	3.351
27	−0.3302	3.686
27	−0.5334	4.144
27	−0.8662	4.374
28	0.930	0.44
28	0.633	0.53
28	0.412	0.27
28	0.277	1.16
28	0.206	2.92
28	0.126	4.40
28	0.053	6.18
28	−0.002	7.86
28	−0.086	8.39
28	−0.239	10.95
28	−0.467	12.37
28	−0.772	13.26
29	0.909	0.20
29	0.620	0.70
29	0.417	2.47
29	0.259	4.72
29	0.185	6.19
29	0.121	7.28
29	0.067	8.12
29	0.006	8.73
29	−0.060	9.82
29	−0.206	11.25
29	−0.427	12.27
29	−0.721	12.59
30	1.080	0.00
30	0.787	0.00
30	0.556	0.00
30	0.412	0.34
30	0.259	1.71
30	0.189	4.41
30	−0.028	7.40
30	−0.100	8.42
30	−0.246	10.13
30	−0.386	11.20
30	−0.897	12.19

Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c
31	1.052	0.02
31	0.625	0.18
31	0.396	1.43
31	0.230	3.61
31	0.135	5.27
31	0.089	6.16
31	0.025	6.97
31	−0.044	7.88
31	−0.113	8.56
31	−0.709	12.06
32	0.856	0.29
32	0.558	1.67
32	0.300	3.78
32	0.187	5.25
32	0.133	5.81
32	0.083	6.38
32	0.036	6.74
32	−0.014	7.18
32	−0.064	7.66
32	−0.164	8.10
32	−0.323	9.73
32	−0.636	10.82
33	0.869	0.02
33	0.653	0.22
33	0.503	0.21
33	0.371	0.69
33	0.227	3.08
33	0.079	5.20
33	−0.070	8.79
33	−0.295	11.68
33	−0.434	12.30
33	−0.584	12.63
33	−0.808	12.70
33	−1.107	12.83
34	1.117	0.00
34	0.818	0.00
34	0.592	0.00
34	0.445	0.00
34	0.300	0.09
34	0.170	1.77
34	0.038	5.66
34	−0.089	9.49
34	−0.229	11.59
34	−0.361	12.50
34	−0.582	12.79
34	−0.879	12.79
35	1.257	0.09
35	0.887	0.07
35	0.483	0.73
35	0.267	3.12
35	0.133	5.33
35	0.062	6.30
35	−0.024	7.90
35	−0.140	9.27
35	−0.310	10.70
35	−0.470	11.59
35	−0.732	12.47
35	−1.153	12.80
36	0.8433	0.01
36	0.5664	0.475
36	0.3454	5.68
36	0.2083	13.065
36	0.0940	17.78
36	0.0406	19.63
36	−0.0203	21.01
36	−0.0838	22.38
36	−0.2108	24.15
36	−0.3581	25.68
36	−0.5842	27.23
36	−0.8890	28.53

TABLE 2.—(*Continued*)

Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c	Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c	Sample No.	Distance from Interface, x, Mm.	Weight Per Cent of Solute, c
37	0.9627	0.00	41	1.2725	0.17	45	0.843	0.09
37	0.6528	0.14	41	0.7340	2.02	45	0.547	0.29
37	0.3912	7.19	41	0.4470	10.92	45	0.279	0.55
37	0.2388	14.75	41	0.2261	17.05	45	0.178	0.64
37	0.1067	19.65	41	0.1778	18.10	45	0.122	0.70
37	0.0508	20.20	41	0.0762	19.45	45	0.067	0.75
37	0.0013	20.76	41	−0.0154	20.79	45	0.004	0.83
37	−0.0356	21.585	41	−0.0724	21.51	45	−0.067	0.90
37	−0.1676	22.73	41	−0.1219	22.03	45	−0.128	0.90
37	−0.3048	24.22	41	−0.5207	24.92	45	−0.269	1.02
37	−0.5207	25.87	41	−0.9576	27.13	45	−0.489	1.23
37	−0.8255	27.43	41	−1.2751	28.07	45	−0.773	1.40
38	0.9144	0.00	42	0.846	0.00	46	0.722	0.07
38	0.6172	1.78	42	0.526	0.02	46	0.457	0.27
38	0.3886	9.00	42	0.304	0.14	46	0.255	0.50
38	0.2642	14.17	42	0.168	0.37	46	0.125	0.70
38	0.1346	17.69	42	0.098	0.55	46	0.074	0.80
38	0.0559	19.81	42	0.032	0.69	46	0.016	0.79
38	−0.0114	20.79	42	−0.018	0.86	46	−0.046	0.90
38	−0.0838	21.81	42	−0.065	1.03	46	−0.132	0.93
38	−0.2413	23.39	42	−0.112	1.20	46	−0.203	1.07
38	−0.3835	25.24	42	−0.221	1.33	46	−0.346	1.19
38	−0.6121	26.30	42	−0.436	1.55	46	−0.571	1.33
38	−0.9144	28.37	42	−0.781	1.63	46	−0.853	1.48
39	1.130	0.02	43	0.826	0.00	47	0.663	0.15
39	0.6960	1.17	43	0.550	0.09	47	0.395	0.31
39	0.5385	5.55	43	0.345	0.17	47	0.236	0.52
39	0.3785	11.88	43	0.206	0.40	47	0.117	0.65
39	0.2299	16.40	43	0.128	0.54	47	0.056	0.75
39	0.0917	19.43	43	0.058	0.70	47	−0.013	0.79
39	0.0241	20.43	43	−0.001	0.83	47	−0.082	0.84
39	−0.0267	21.20	43	−0.055	0.97	47	−0.145	0.91
39	−0.1575	22.72	43	−0.105	1.10	47	−0.234	0.99
39	−0.2718	23.68	43	−0.207	1.21	47	−0.401	1.13
39	−0.3276	24.08	43	−0.392	1.39	47	−0.628	1.29
39	−0.4877	25.08	43	−0.678	1.54	47	−0.909	1.41
39	−0.7518	26.51						
40	0.9271	0.01	44	0.673	0.05			
40	0.6350	0.295	44	0.396	0.23			
40	0.427	1.33	44	0.238	0.43			
40	0.273	6.035	44	0.113	0.64			
40	0.1245	12.89	44	0.046	0.67			
40	0.0584	17.15	44	−0.031	0.74			
40	0.0089	19.72	44	−0.109	0.90			
40	−0.0432	21.15	44	−0.191	1.01			
40	−0.1867	24.90	44	−0.373	1.20			
40	−0.3378	26.71	44	−0.442	1.28			
40	−0.5664	28.42	44	−0.683	1.38			
40	−0.8712	29.93	44	−0.943	1.52			

in which c_0 is the initial concentration of the solute in the high-concentration alloy, c is the concentration of the solute after diffusion at distance x from the interface after the time interval t, ϕ is the Gauss error function, and D the desired diffusion coefficient.*

The present data were first analyzed by this method and an example of the calculation will be given in illustration. In sample 2 the core alloy contained 8.50 per cent Al (Table 1) which is c_0. The value of c is obtained from the diffusion penetration curve (Fig. 1) plotted from the data of Table 2. To read c, a distance of $x = 0.1$ mm. (0.01 cm.) has been arbitrarily selected. This distance is measured in the direction of the copper plate, not from the original interface but from the point at which the penetration curve crosses the 50–50 composition (4.25 per cent Al) designated in Fig. 1 as the "Grube interface." At the point indicated, c is seen to have a value of 2.3 per cent Al. The value of 38.40 days

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* The diffusion coefficient represents the amount of substance in grams diffusing in one second across an area of 1 sq. cm. through a unit concentration gradient (ref. 1, p. 3). Dimensional analysis shows this coefficient to have the dimensions of length² divided by time.

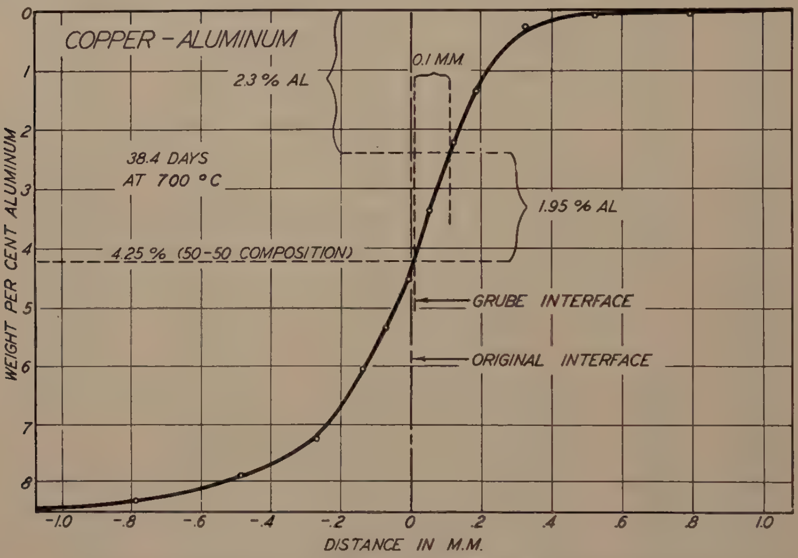

Fig. 1.—Diffusion-penetration curve illustrating Grube method of computing diffusion coefficient.

for t and the temperature of 700° C. are taken from Table 1. Rewriting equation 2, we have

$$\frac{\frac{c_0}{2} - c}{\frac{c_0}{2}} = \phi\left(\frac{x}{2\sqrt{Dt}}\right) \tag{3}$$

and substituting obtain

$$\frac{4.25 - 2.3}{4.25} = 0.459 = \phi\left(\frac{0.01}{2\sqrt{38.4D}}\right)$$

In a table of the Gauss error functions (probability integrals), it is found that $0.459 = \phi\,(0.432)$.

Thus

$$\frac{0.01}{2\sqrt{38.4D}} = 0.432$$

and

$$D = 0.349 \times 10^{-5} \text{ sq. cm. per day}$$

or, converting days to seconds,

$$D = 0.404 \times 10^{-10} \text{ sq. cm. per second}$$

It has been shown by Grube, and it can be verified from the present data, that the calculated value of D is a function of the arbitrarily selected distance x, and that therefore D varies with concentration. It must accordingly be concluded that the diffusion coefficients computed by the Grube method are only approximately correct, and that the Matano method of analyzing the data should be used. This may be seen in Table 3, in which are given D values calculated by each method at identical concentration values for Cu-Al alloys at various temperatures. While comparable D values agree as to order of magnitude, their differences are appreciable.

TABLE 3.—*Comparison of D Values for Diffusion in Cu-Al System as Computed by Grube and Matano Methods*

Sample No.	Temperature, Deg. C.	Time, Days	$D \times 10^{-10}$ Sq. Cm. per Sec.	
			At x = 0.1 Mm., Grube Method	At Corresponding Concentrations, Matano Method
1	700	22.42	0.57	0.55
2	700	38.40	0.43	0.56
3	699	86.96	0.41	0.30
4	755	7.13	1.89	1.6
5	750	14.00	2.24	1.8
6	903	1.08	22.63	12.8

Matano employed the following statement of Fick's law:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) \qquad [4]$$

which provides for the possibility of a variation of D with c. The boundary conditions for the application of the solution of this equation to the present data are the same as for equation 1.

In order to reduce equation 4 to a usable form, it is necessary to make some assumption concerning the relationship existing between x, the distance between the interface and the point at which the concentration is measured, and t, the time interval of diffusion. Experimentally, Matano had shown that the relation $\lambda = x/\sqrt{t}$ where λ is a constant for any given concentration of the solute, is at least approximately correct. A test of its validity is illustrated in Fig. 2, where the x distance has been plotted as a function of the square root of the time for a series of concentrations of aluminum diffusing into copper at 700° C. The readings are taken from the measurements on samples 1, 2, and 3. If λ is truly a constant, all of the points corresponding to a single concentration should fall upon a straight line passing through the origin; Fig. 2 shows this to be approximately true.

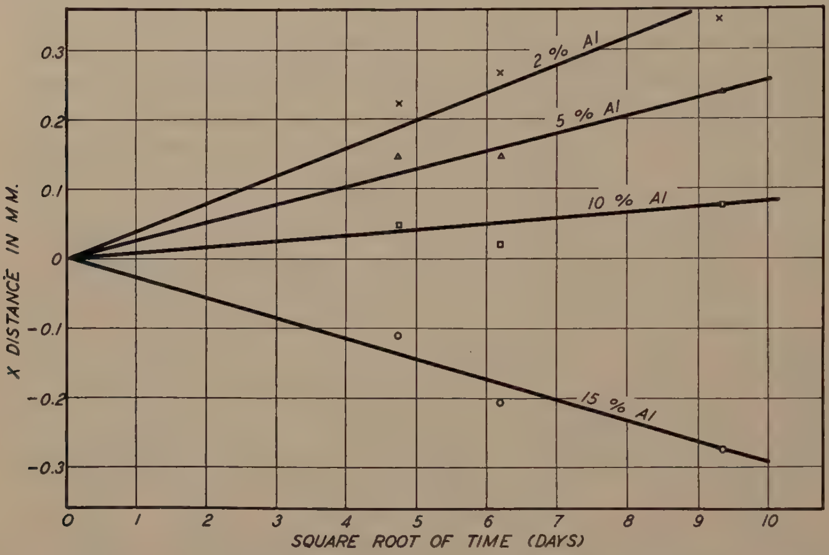

FIG. 2.—TEST OF VALIDITY OF RELATIONSHIP $\lambda = \frac{x}{\sqrt{t}}$ IN CU-AL SYSTEM AT 700° C.

For the boundary conditions of these experiments, the differential expression may be solved for D, obtaining

$$D = -\frac{1}{2}\frac{d\lambda}{dc}\int_0^c \lambda dc, \text{ with the condition that } \int_0^1 \lambda dc = 0.$$

Since the time t is a constant for any experimentally determined penetration curve, the expression may be further simplified to

$$D = -\frac{1}{2t}\frac{dx}{dc}\int_0^c xdc = \frac{1}{2t}\frac{dx}{dc}\int_c^1 xdc, \text{ with the condition that } \int_0^1 xdc = 0. \quad [5]$$

In this form, D may be evaluated from the penetration curve by a graphical method, for dx/dc is simply the slope of the penetration curve at the concentration c, and $\int_0^c xdc$ is the area enclosed by the curve, the interface, and the limits of concentration 0 and c. The interface used in defining the area $\int_0^c xdc$ is not the original interface existing prior to the operation of the diffusion process, but is defined as the surface through which an equal number of the two kinds of atoms have passed in opposite directions. Graphically it is the value of x that so intersects the penetration curve as to equalize the two areas on either side. The concentration is, of course, expressed in atomic fraction. This definition fulfills the requirement of the condition $\int_0^1 xdc = 0$, attached to equation 5.

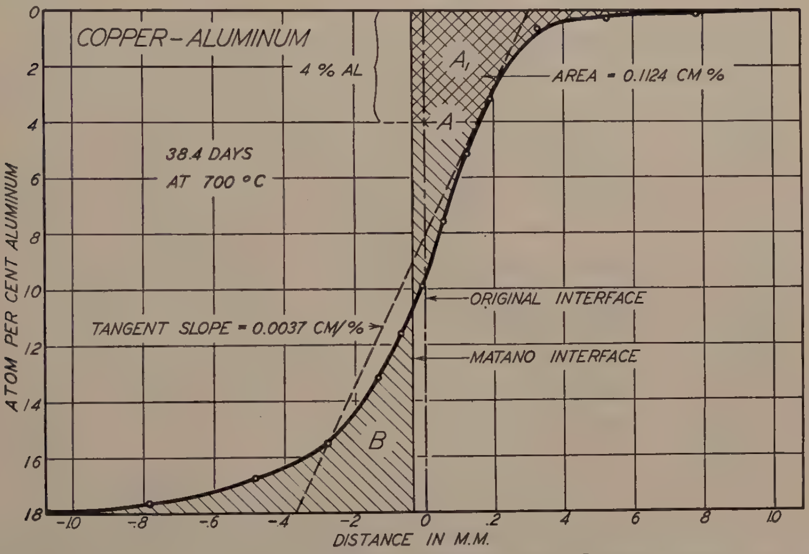

FIG. 3.—DIFFUSION-PENETRATION CURVE ILLUSTRATING MATANO METHOD OF COMPUTING DIFFUSION COEFFICIENT.

The application of the Matano method of evaluating D is demonstrated in Fig. 3 for the case of sample No. 2. Here the penetration curve has been plotted in atom per cent in accordance with the requirements of the solution. In order to locate the Matano interface, a vertical line is drawn in such a manner that the crosshatched areas A and B are made equal. This has been done by "trial and error" comparing the two areas either by the use of a planimeter or by counting squares on the graph paper. For the purpose of illustration, D will be computed at 4 atom per cent of aluminum. The double hatched area A_1 lying between the 0 and 4 per cent Al horizontals is found to be 0.1124 cm. per cent. This is the value of the term $\int_0^{0.04} xdc$. At the point where the penetration curve crosses 4 per cent, its tangent is drawn by eye. The slope of the tangent dx/dc is read directly as 0.0037 cm. per per cent. The time of diffusion for sample No. 2 was 38.4 days, whereby the value of the term $1/2t$ is seen to be 0.01303 days^{-1}. By taking the product of these three factors, the value of D is found.

$$D = 0.01303 \times 0.0037 \times 0.1124 = 0.542 \times 10^{-5} \text{ sq. cm. per day}$$

or, converting to seconds,

$$D = 0.627 \times 10^{-10} \text{ sq. cm. per second}$$

If this procedure is reproduced for a series of values of increasing c, it will be found that D increases, slowly at first and then more rapidly, as c approaches its limiting value. The calculation of D at concentrations greater than that at the Matano interface is accomplished by the same sequence of operations as at lower concentrations except that the areas are measured in the B area between the test composition and the maximum solute concentration of the system. A plot of the relation between concentration and D for sample No. 2 is given in Fig. 4.

In Figs. 4 to 9 inclusive, the values of D are plotted as a function of concentration for the solutes aluminum, beryllium, cadmium, silicon, tin and zinc. These have been computed by the Matano method in exactly the manner described above. All curves drawn with solid lines are found by direct computation, with extrapolated portions of the curves indicated by dashes. One exception to this practice is to be noted in the case of Fig. 9, where the curves for the 13 per cent Zn alloy are plotted with a dotted line to distinguish them from those obtained from the 30 per cent Zn alloys.

ERRORS IN THE DETERMINATION OF D

Because of the large number of individual operations involved in the determination of a value of the diffusion coefficient, and because of the extent to which the measurements depend upon manual skill and judgment, it is not easy to estimate the probable degree of accuracy of this work, though the sources of error can be enumerated and individually appraised. All samples that were damaged in handling, or that were ultimately found to be defective in any way, were discarded; about 15 samples were eliminated on this basis. The sources and probable extent of each of the errors that may have occurred are listed below. Many of these may mutually cancel, so that the net error in most cases will be less than the sum of the errors.

Presence of Impurities.—There can be no doubt that the presence of impurities will affect the D value; the extent of the effect will be roughly proportional to the ratio of the impurity to the solute in the core alloy. For the zinc alloys, two different core compositions were used. The 30 per cent Zn alloy contained 1.09 per cent impurities, whereas the the 13 per cent Zn alloy contained 0.12 per cent. Thus the impurity to solute ratio in the first case is 0.034 and in the second 0.008. In Fig. 9 the D versus concentration curves for both alloys are plotted together. Although the average difference in the D values between the two alloys is less than the scatter among the values from a single alloy,

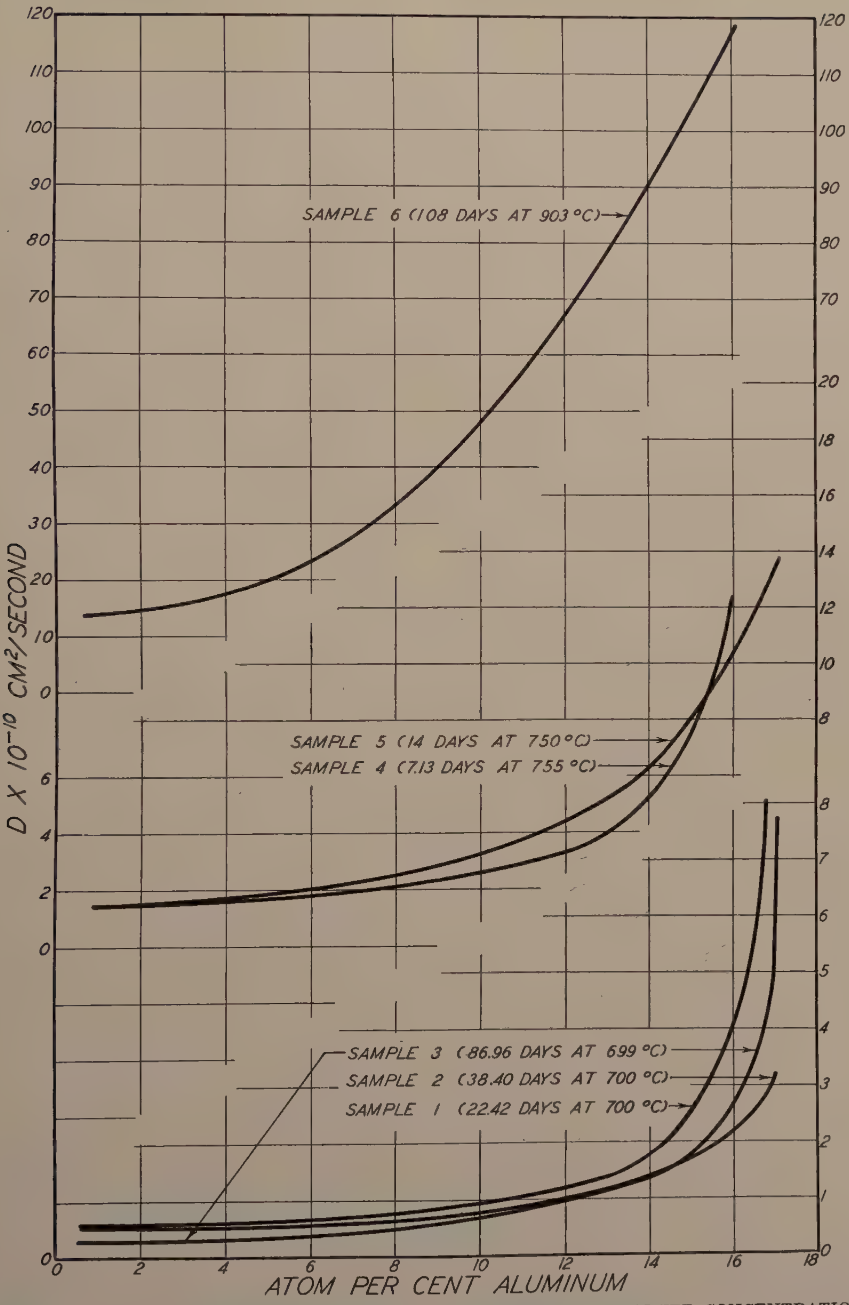

Fig. 4.—Diffusion coefficient plotted as function of solute concentration for Cu-Al alloys at various temperatures.

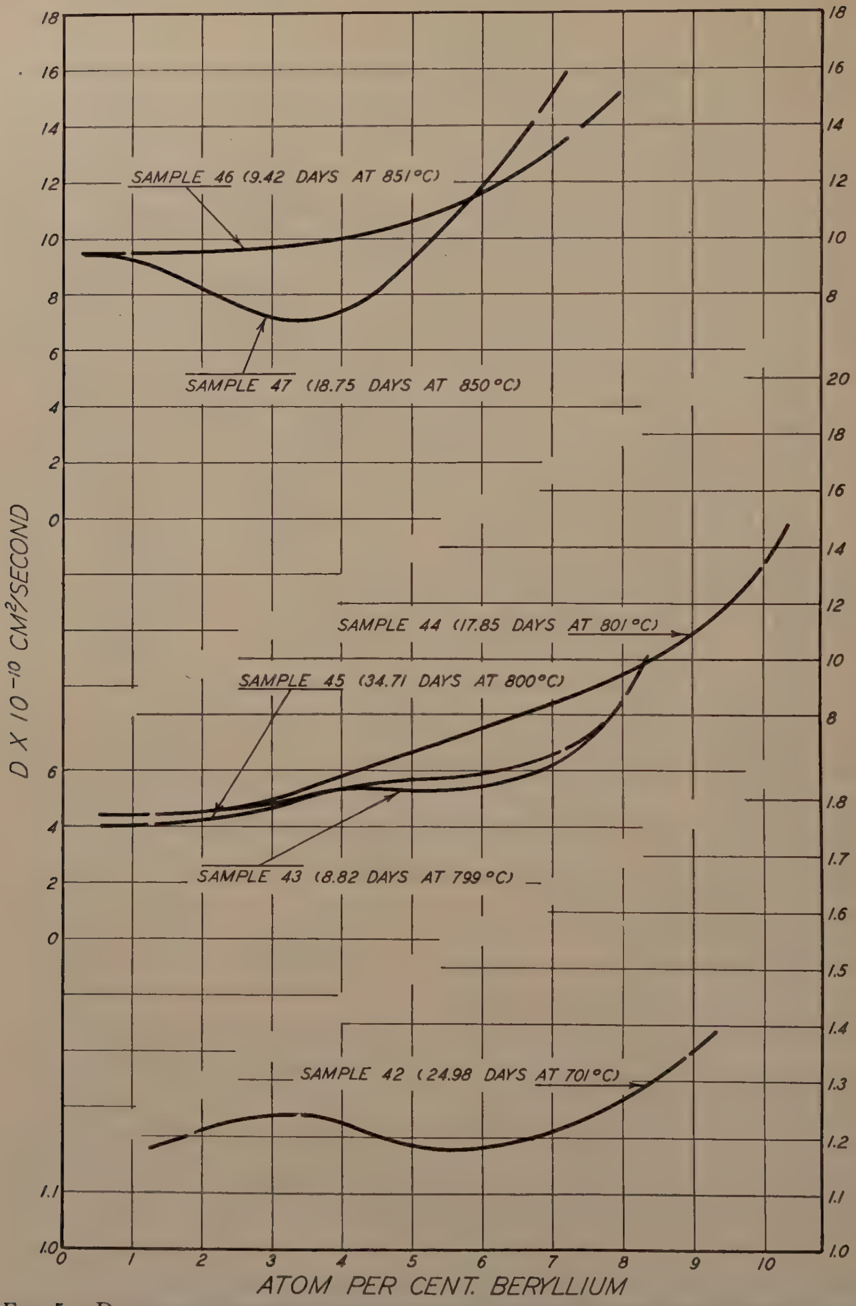

FIG. 5.—DIFFUSION COEFFICIENT PLOTTED AS FUNCTION OF SOLUTE CONCENTRATION FOR CU-BE ALLOYS AT VARIOUS TEMPERATURES.

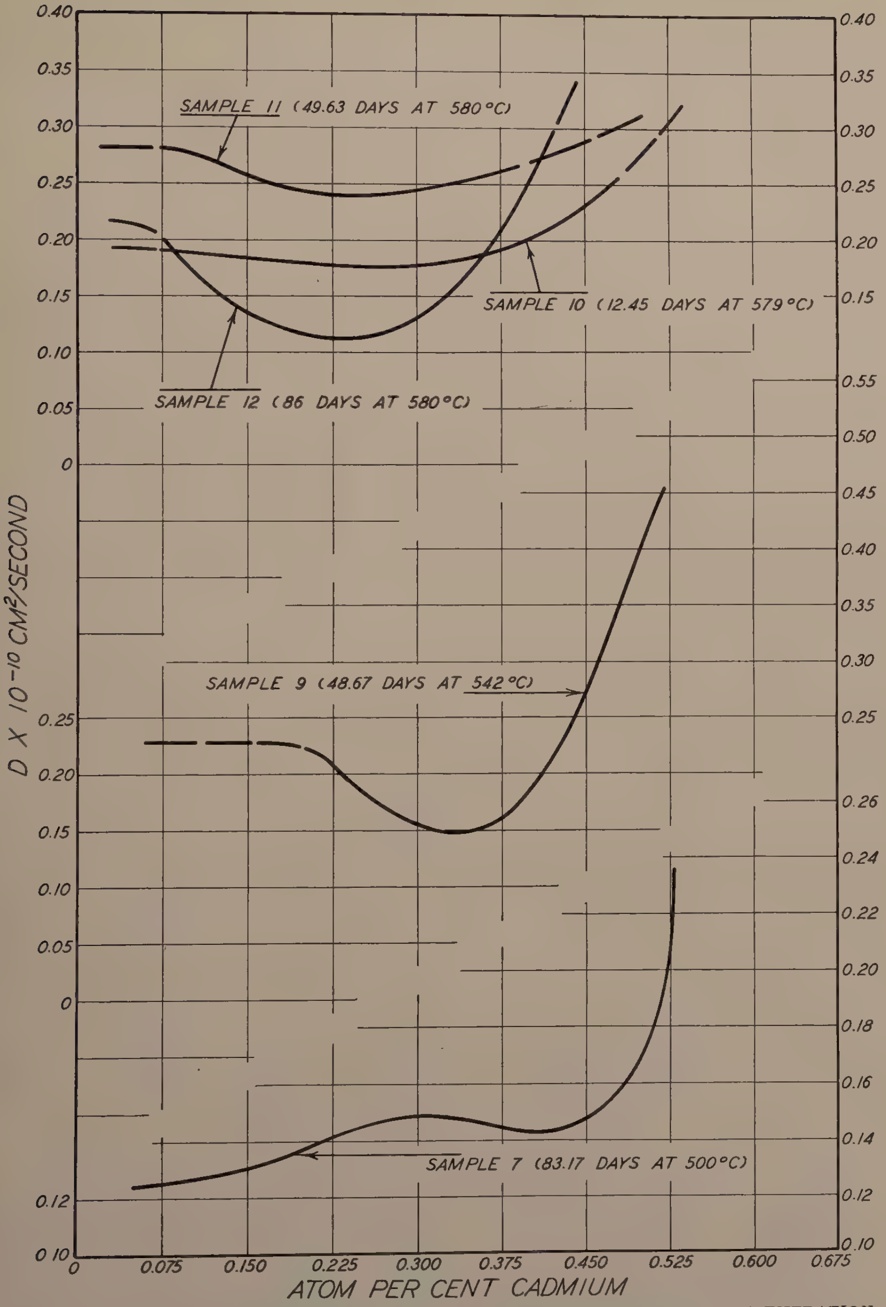

FIG. 6.—DIFFUSION COEFFICIENT PLOTTED AS FUNCTION OF SOLUTE CONCENTRATION FOR CU-CD ALLOYS AT VARIOUS TEMPERATURES.

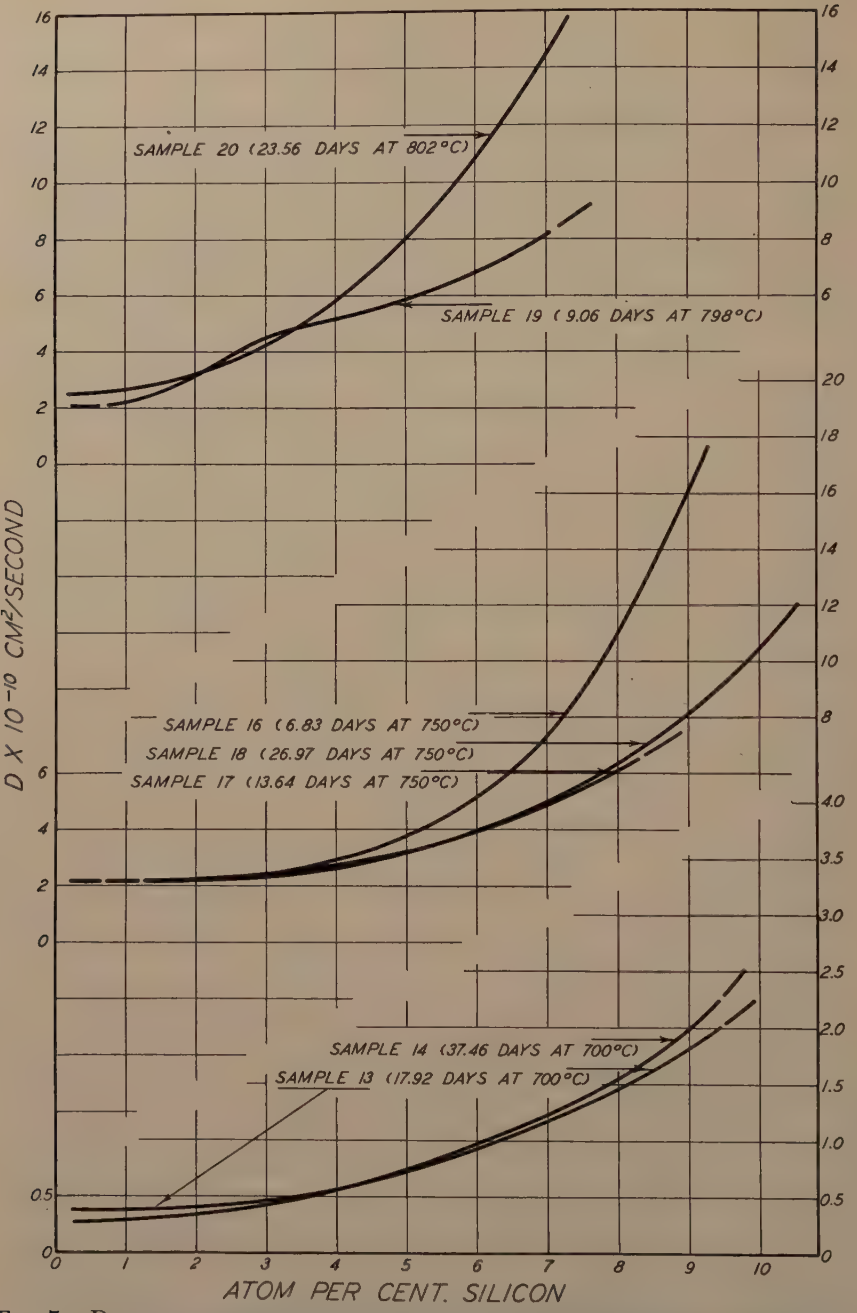

FIG. 7.—DIFFUSION COEFFICIENT PLOTTED AS FUNCTION OF SOLUTE CONCENTRATION FOR Cu-Si ALLOYS AT VARIOUS TEMPERATURES.

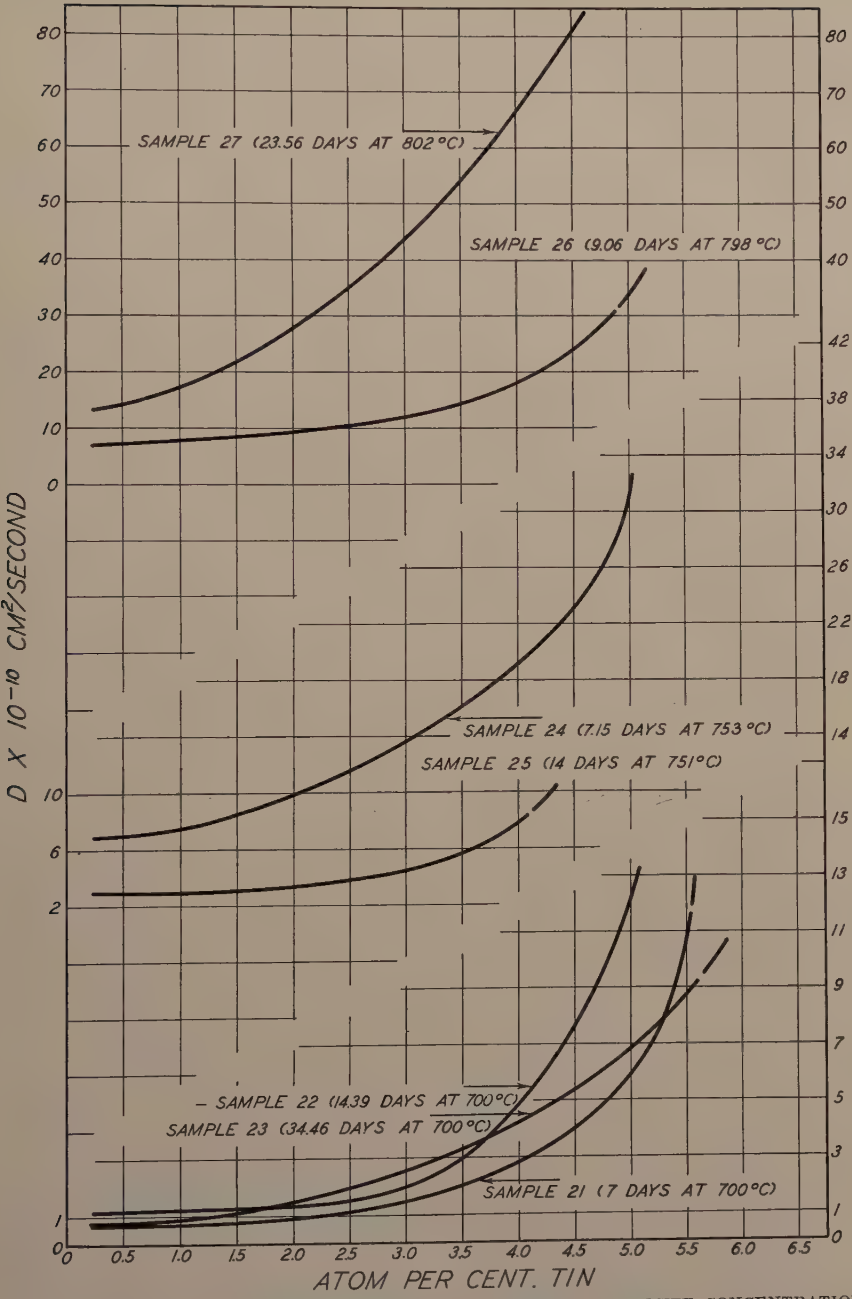

FIG. 8.—DIFFUSION COEFFICIENT PLOTTED AS FUNCTION OF SOLUTE CONCENTRATION FOR CU-SN ALLOYS AT VARIOUS TEMPERATURES.

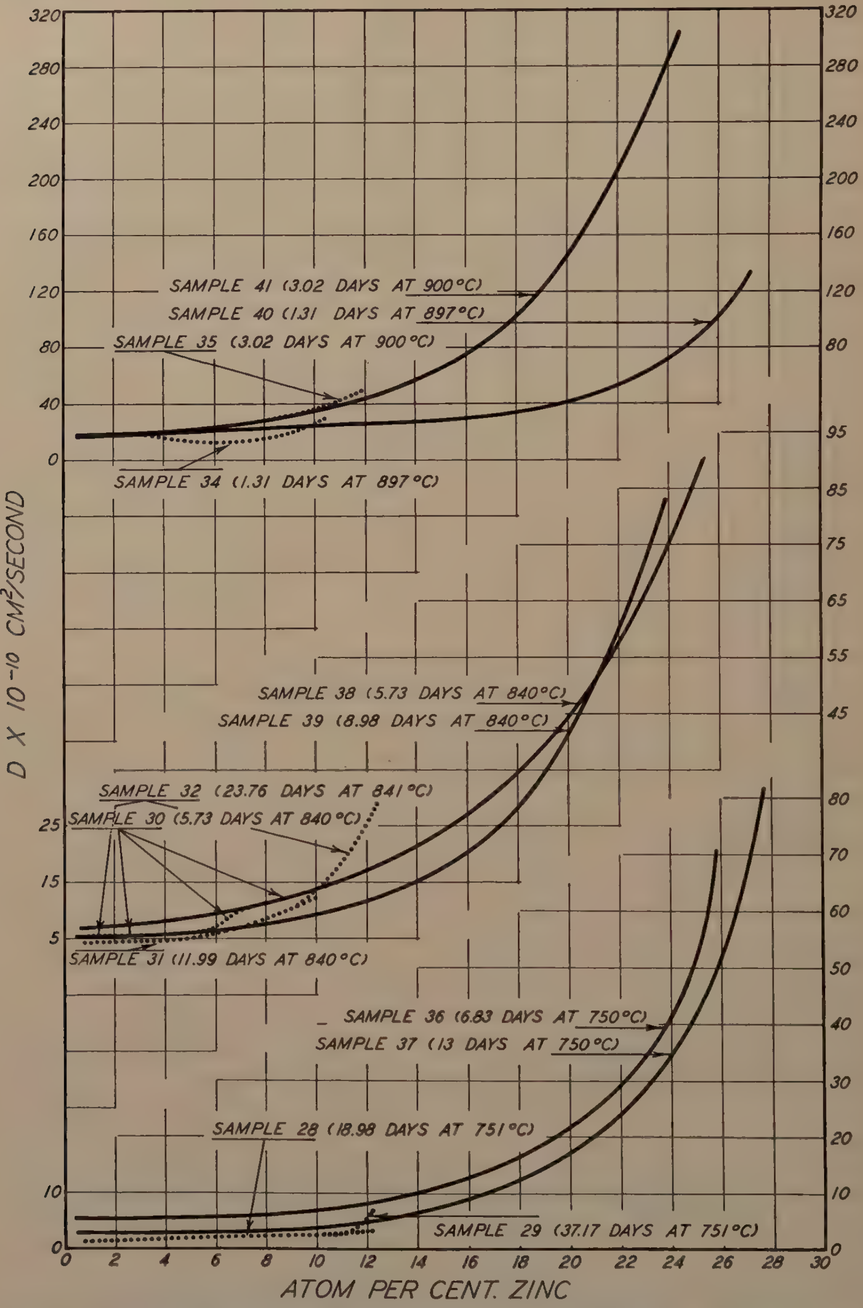

FIG. 9.—DIFFUSION COEFFICIENT PLOTTED AS FUNCTION OF SOLUTE CONCENTRATION FOR Cu-Zn ALLOYS AT VARIOUS TEMPERATURES.

it may be seen that there is a slight tendency for the 30 per cent Zn alloy to show a high D value.

Inhomogeneity.—To what extent inhomogeneities may have vitiated the final results is indeterminate. Since, however, all analyses were made over a considerable length of sample, it seems most probable that such effects have been averaged out.

Grain Size.—No attempt has been made to evaluate the influence of grain size upon the measurements here reported. The grain size of the copper plates was approximately the same in all cases, and there was no marked difference in the grain sizes of the core alloys, as may be seen in the photomicrographs in Figs. 10, 11 and 12. The microstructures of the alloys taken after diffusion show that recrystallization and grain growth had taken place in the diffusion zone (Fig. 12 particularly). There is no evidence in copper-base alloys for a more rapid diffusion along grain boundaries; though α Cu-Zn alloys when heated in a vacuum lose zinc more rapidly at the grain boundaries than from areas away from boundaries, this effect results from shrinkage which cleaves the aggregate at the boundary rather than from an enhanced rate of diffusion at the boundary.[1] The results of Bugakov and Rybalko[12] are probably to be explained in this way. Nevertheless, studies on grain-boundary diffusion in these alloys are much needed. If there is a minor grain-boundary effect, the results given here must be taken as averages of general applicability to commercial alloys.

Non-adherence of Plates.—Every precaution was taken to obtain clean interfaces between the alloy cores and the copper plates; nevertheless, the photomicrographs (Figs. 10, 11 and 12) show rings of dots along the original interfaces and in some cases additional rings representing the progress of plating at a time when the operation was interrupted for inspection. The size of these dots has evidently been greatly exaggerated in etching (Fig. 11), for no markings could be seen in most of the unetched samples. In the majority of cases the deposits seem to have become spheroidized, and in this form probably have a minimum influence upon the rate of the diffusion process. Occasionally, however, the plates seem to have separated from the cores, for in a few instances during machining the layer of copper next to the interface peeled off; all samples in which this tendency was at all pronounced were discarded. One sample possessing this defect to a very minor degree has been included (silicon-alloy sample No. 19), with the results reported. The effect upon the D value seems to have been small at low concentrations of silicon but amounts to an extensive lowering of D at high concentrations. It is not certain that this behavior is to be traced to interface imperfection, but no other defect was identified.

Uncertainty of Dimensions.—The diameters of the bars and the thickness of the layers taken for analysis were measured to an accuracy of

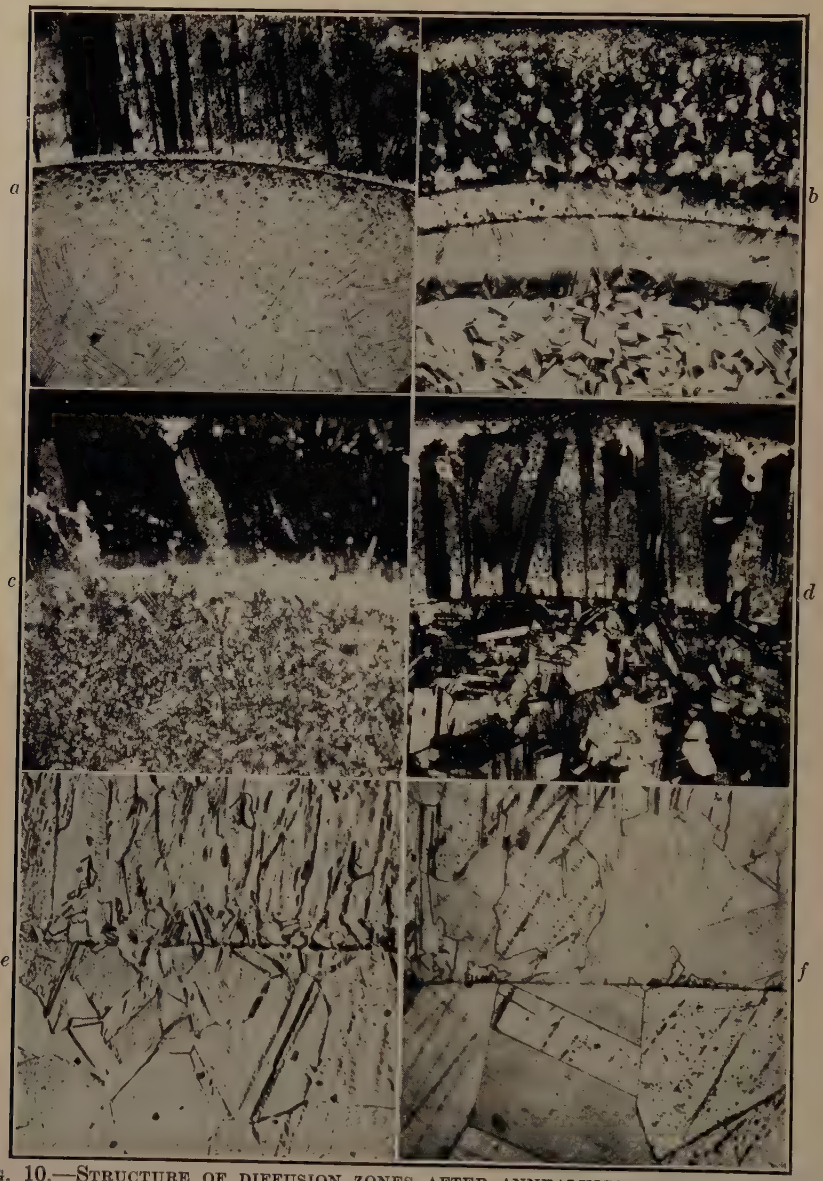

FIG. 10.—STRUCTURE OF DIFFUSION ZONES AFTER ANNEALING; COPPER ABOVE AND ALLOY BELOW.

a. Sample 6, Cu-Al, etched with HNO_3, × 20.
b. Sample 14, Cu-Si, etched with HNO_3, × 20.
c. Sample 27, Cu-Sn, etched with HNO_3, × 20.
d. Sample 38, Cu-Zn, etched with HNO_3, × 20.
e. Sample 7, Cu-Cd, etched with $CrO_3 + H_2O$, × 300.
f. Sample 43, Cu-Be, etched with HNO_3, × 90.
Original magnifications given; reduced ¼ in reproduction.

±0.0003 in. The precision of this measurement, therefore, is equal to that of plotting the penetration curves upon graph paper on which the smallest divisions represent 0.005 mm., and thus no appreciable error may be assigned to this source.

Eccentricity of Turning Centers.—Because of the necessity of relocating the turning centers in the diffusion bars after the heat-treatments, some eccentricity may have been introduced. This could invariably be detected during machining, for the color change in the alloys at the interface was generally quite distinct, and any eccentricity in the sample was made evident by a variation in the color around the circumference. All bars in which this defect was found were discarded.

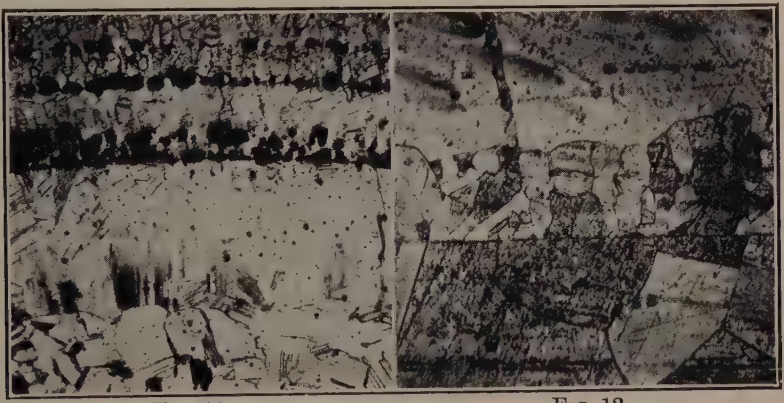

FIG. 11. FIG. 12.

FIG. 11.—SAMPLE 14, CU-SI, ETCHED WITH HNO_3, × 40.
Showing distribution of impurities at interface. Particle sizes very greatly exaggerated by overetching.

FIG. 12.—SAMPLE 6, CU-AL, ETCHED WITH HNO_3, × 175.
Showing recrystallization in diffusion zone.
Original magnifications given; reduced ¼ in reproduction.

Inadequate Thickness of Sample.—The methods used for calculating *D* from the concentration-penetration curves require that none of the solute metal reach the outside of the copper plate, and that the composition at the center of the core remain unchanged. Spectroscopic traces of the diffusing metals did, of course, reach the outside of the samples, but in no case were chemically detectable traces of the solute found nearer to the surface than the middle of the copper plates. The cores were so much thicker than the plates that depletion in solute at the center was infinitesimal.

Dimensional Changes during Annealing.—A record has been kept of the external dimensions of the samples before and after heat-treatment. This shows that practically all of the bars suffered lengthwise expansions of between 0.001 and 0.005 in. per in. The radial expansion was negligible. In a number of cases the linear expansion of the plate differed from that of the core. The difference was greater in the alloys of cadmium, silicon, tin and zinc; less in alloys of beryllium, and unmeasurable in that of aluminum. In no case was the difference greater than a few ten-thousandths of an inch per inch. The error introduced from this source is difficult to appraise, but is doubtless small, owing to the minuteness of the effect.

Variations in Annealing Temperature.—The effect upon the value of D of errors in the temperature measurement is greater at low temperatures than at high, is more important in some alloys than in others, and varies with the solute concentration. The maximum error possible in the systems studied seems to be about 3 per cent of the D value per degree of temperature error, except near the maximum solute concentrations, where larger errors may be found. The temperatures as recorded in Table 2 are probably correct to 1°C. The thermocouples were checked frequently against the melting points of high-purity metals, and all temperature measurements were made with a type K potentiometer.

Uncertainty of Time Measurements.—Since the major part of the error in time in this research is related to the uncertainty in the time required for the samples to reach the annealing temperature and to cool down to room temperature, this inaccuracy will have been most significant when the time interval of diffusion was short. It is believed that errors introduced into the D values in this way do not exceed 1 per cent. It can be shown that no detectable diffusion could have taken place in these samples at room temperature during the period that elapsed between the diffusion anneal and chemical analysis.

Vapor-phase Contamination.—In spite of the precautions taken, it is certain that the samples were subject to a certain amount of contamination during the annealing treatments. Carbon, oxygen and copper were always present in the neighborhood of the samples. None of the solute metals except silicon are at all likely to form carbides under the conditions of the experiments, and it is highly doubtful that silicon carbide could have formed. All of the solute metals oxidize readily. For this reason, carbon was introduced into the annealing chambers, but it was not wholly efficient in eliminating oxygen, especially when the treatments were of long duration. A tarnish or thin scale was often formed on the surface of the bars, but no oxide visible under the microscope was found within the diffusion zones. The effect of the intrusion of oxygen upon the D value would undoubtedly be to raise it, for the solute-metal gradient would be increased by the withdrawal of the metal from solution, and the oxide and free metal would appear together in the chemical analysis.

Accuracy of Chemical Analysis.—The accuracy of the D values depends upon the accuracy of the chemical analyses more than upon that of any other measurement. The relation between analytical accuracy and the error in D is a complex function depending upon: (1) the difference between the core and plate compositions, (2) the concentration range in which D is being measured, and (3) the concentration gradient existing there. Where there is a large difference between the core and plate compositions, where D is being measured at a concentration near the middle of the penetration curve, and where the concentration gradient is of intermediate steepness, the value of D will be least affected by errors in the chemical analysis. Under the most favorable conditions the error in the results which might have been introduced by an analytical error of 0.1 per cent varies from about 5 per cent of D in the Cu-Zn alloys to 50 per cent in the Cu-Cd alloys. Near the limits of the concentrations measured, the sensitivity to analytical errors becomes so great that a similar inaccuracy might change the value of D by several thousand per cent or more. For this reason, the D values near zero and the maximum concentrations of the solute show little agreement from sample to sample and have not been plotted in Figs. 4 to 9 inclusive. In almost every case, the D versus concentration curves turned sharply up or down at the ends, with no apparent reason other than that of the random direction of the analytical error. Sometimes the irregularities extended throughout the course of the D versus concentration curves, as is all too apparent in the curves for the cadmium and beryllium alloys. Here the solute concentrations were extremely low when expressed in weight per cent, and the error was correspondingly great. Perhaps the best general test of the reliability of the analytical data lies in the smoothness of the resulting concentration-penetration curve. An example of a typical curve has been shown in Figs. 1 and 3. The cadmium and beryllium curves were less regular.

Location of Interface.—Small mistakes in the location of the Matano or Grube interfaces make relatively little difference in D, unless the concentration-penetration curve is very steep. In the analysis of the data reported here, the maximum error in D that might accrue from this source is about 20 per cent for an error of 0.01 mm. in the interface location on the steepest curves. Ordinarily the error must have been under 5 per cent of D. The shifting of the interface has the effect of rotating the D versus concentration curve about some intermediate concentration value.

Location of Tangent.—All visual locations of the tangents to the penetration curves have been checked by at least two persons. Within the intermediate concentration ranges, the readings seem to be reliable to within a few per cent, but near the concentration limits where the penetration curves approach parallelism with the distance axis, little confidence can be placed in the values of the estimated tangents. This is not very troublesome, for the range in which the error is great corresponds with that of the maximum error in chemical analysis. The accuracy of D varies directly as the accuracy of the tangent measurement.

Area Measurements.—The areas under the penetration curve were measured with a planimeter. They are undoubtedly accurate to within 2 or 3 per cent, except near zero and near the maximum concentration where errors in the area under a flat curve become appreciable. The certainty of the measurement is generally greater at low than at high solute concentrations. All area readings were checked twice.

Assumption of Planar Instead of Radial Diffusion.—It has been mathematically demonstrated that the treatment of the data as though the diffusion were taking place between two flat plates instead of radially in a cylinder has had no appreciable effect upon the results. Were the bars of a much smaller diameter, a modification of the analytical treatment would have been required.

CRITICAL EVALUATION OF RESULTS

Viewing as a whole the analysis of errors, it becomes apparent that the factors of critical importance are: (1) temperature control, (2) chemical analysis, and (3) determination of the slopes of the tangents to the penetration curves. In most of the cases of Figs. 4 to 9 the lack of agreement among check samples is traceable to errors in one or more of these operations. Generally speaking, it is true that the D values are most unreliable at the maximum and at the minimum concentrations.

Surprisingly good agreement has been obtained among the curves for the Cu-Al alloys (Fig. 4). As is to be expected, the agreement is best at the intermediate concentrations of aluminum. Judging from the rapidity with which the 700° curves turn upward near 17 per cent Al, the D values may be too high in this range.

There is a marked disagreement among corresponding curves for the Cu-Be alloys (Fig. 5), and the forms of the curves are not as regular as others. This is no more than should be expected, however, because the maximum concentration of the system was less than 2 weight per cent of beryllium, and a magnification of the analytical errors is to be anticipated under such circumstances.

The same comments apply to the Cu-Cd curves (Fig. 6), but to an even greater degree, for in this instance the largest cadmium concentration was near 1 per cent. The scatter among the results is so pronounced that the curves can be taken to indicate only the order of magnitude of the diffusion coefficient.

At low concentrations, the curves for the Cu-Si alloys (Fig. 7) exhibit very satisfactory agreement, but rather large deviations appear at the higher concentrations. Because of a known defect in sample 19, it is believed that the data of sample 20 are the more reliable for this pair. The curves of samples 17 and 18 almost superimpose and therefore are to be preferred to that of sample 16.

The evaluation of the results of the Cu-Sn alloys (Fig. 8) is most difficult. At 700° C. fairly good agreement among the D versus concentration curves is found, but at 750° and 800° C. there is a marked lack of agreement. Unfortunately, no experimental error of any magnitude has been identified among the Cu-Sn samples, so that it is impossible to point with any degree of certainty to the most dependable results. If, however, it is true, as it appears to be, that the D values should be the same for all alloys at the zero solute concentration, the lower of each set of curves is to be preferred. Accordingly, in all of the subsequent discussion the lower curves have been assumed to be the more nearly correct.

Among the Cu-Zn curves (Fig. 9), the agreement is again surprisingly good. No doubt this is attributable to the high maximum zinc content of the core alloys. The fact that the results obtained from the 13 per cent Zn samples are slightly lower than those from the 30 per cent alloys has already been explained upon the basis of impurities in the latter. The agreement between the curves of samples 35 and 41 justifies giving them preference over the lower curve of sample 40.

CALCULATION OF Q

The variation in D with temperature may be expressed by the equation

$$D = A \times e^{-Q/RT} \qquad [6]$$

in which A is a constant, R the gas constant, T the absolute temperature, and Q the activation heat of diffusion. In logarithmic form this expression is

$$\log_e D = \log_e A - Q/RT$$

whence it becomes evident that Q/R is the slope of the straight line obtained by plotting the natural logarithm of D versus the reciprocal of the absolute temperature. Because D is a function of the solute concentration, it follows that Q may be related to the concentration. It is important, therefore, that the values of D used in plotting the log D versus $1/T$ curve correspond to a single solute concentration.

In Fig. 13 the log D versus $1/T$ curves for the Cu-Al alloy at a series of concentrations have been plotted. As a matter of convenience, the logarithm to the base 10 of D has been used instead of the natural logarithm. To read the value of Q from each of these curves, it is necessary only to multiply the slope by the product of the Napierian base and the gas constant (approximately 4.58).

From the fact that the log D versus $1/T$ curves for various concentrations of aluminum are not parallel, it is obvious that Q varies with the concentration. The relationships existing between Q and the solute concentrations for all of the systems studied are summarized in Fig. 14.

All of the curves of Q versus concentration have been derived from the diffusion coefficients by the method described above. In so doing it has

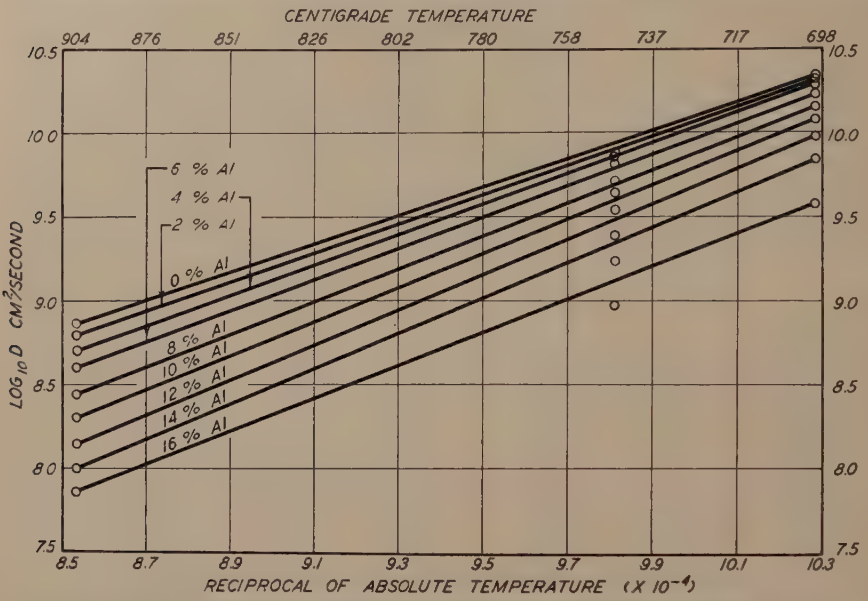

FIG. 13.—PLOT OF $\log_{10} D$ VERSUS $1/T$ FOR VARIOUS CONCENTRATIONS OF CU-AL SYSTEM. ILLUSTRATING METHOD OF COMPUTING Q.

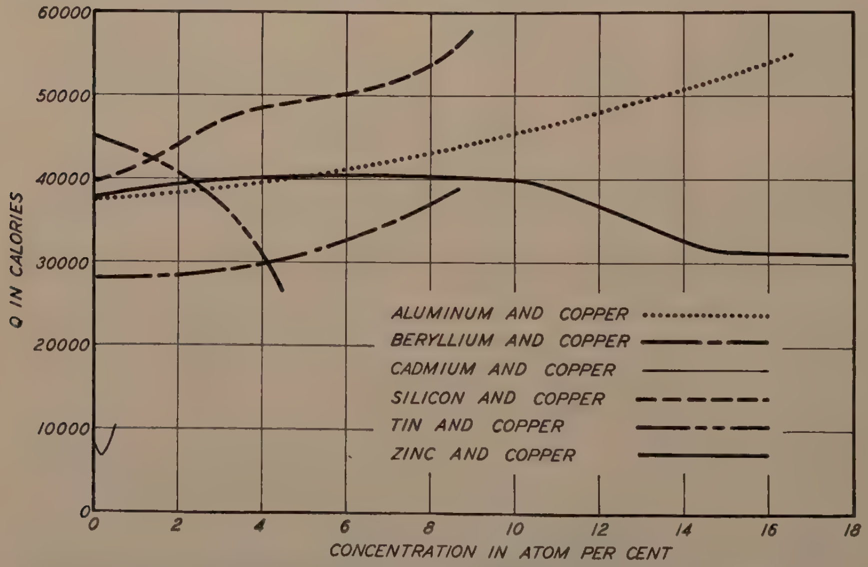

FIG. 14.—RELATIONSHIP BETWEEN Q AND CONCENTRATIONS FOR THE SYSTEMS CU-AL, CU-BE, CU-CD, CU-SI, CU-SN AND CU-ZN. (See note under Fig. 15.)

been necessary to select definite values of D from the D versus concentration curves of Figs. 4 to 9. An effort has been made to take the best average values of D from each group of curves, but owing to the irregularity of many of the data the selection has often been quite arbitrary. In all cases the log D versus $1/T$ curves have been drawn through the most widely separate points on the temperature axis. This was done because it was felt that greater accuracy could be thus obtained, but it should be mentioned that the points at intermediate temperatures rarely fell upon the straight line drawn in this way, as can be seen in Fig. 13. This latter observation may indicate a variation of Q with temperature or simply an inaccuracy in the results. Special mention should be made also of the case of the Cu-Sn alloys, for in these the lower of each pair of D versus concentration curves was used for reading the D values. No great amount of certainty can be attached to the Q versus concentration curves for the Cu-Sn system. Owing to the special difficulties in making precise measurements of D in the systems Cu-Be and Cu-Cd the Q curves for these systems are wholly uncertain.*

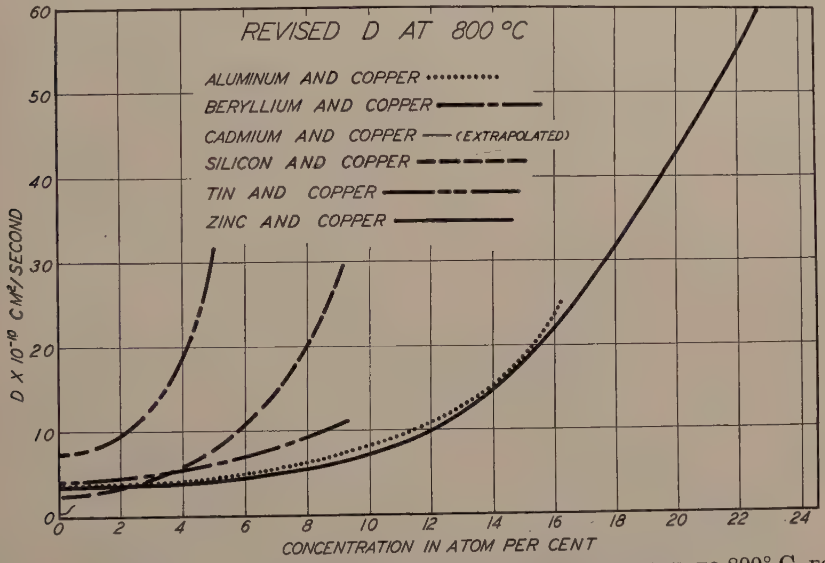

FIG. 15.—SELECTED AVERAGE DIFFUSION COEFFICIENTS INTERPOLATED TO 800° C. FOR SYSTEMS CU-AL, CU-BE, CU-CD, CU-SI, CU-SN AND CU-ZN.

The copper-cadmium curve is shown in Figs. 14 and 15 near the origin, extending to less than one atomic per cent cadmium.

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* Fig. 15 gives the values of D at 800° C. as a function of concentration for the six systems. The values of D at any other temperature may be obtained by reading D at 800° for a particular concentration, reading Q from Fig. 14 for the same concentration and employing equation 6. Thus, if the value of the diffusion coefficient at 700° C. is desired, we have $\log_e D_{700°} = \log_e D_{800°} + \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, in which, of course, T_2 and T_1 represent absolute temperatures; namely, $800 + 273$ and $700 + 273$, respectively.

The log D versus $1/T$ curves plotted from the diffusion-concentration curves extrapolated to zero copper for each of the six systems are given in Fig. 16. These curves have nearly the same slope, except those of the Cu-Be and Cu-Cd alloys, for which the data are not precise, and thus suggest that all values of Q extrapolated to zero copper are identical.

DISCUSSION

From the discussion of the validity of the data, it may be seen that a number of conclusions can be drawn for which there is a high degree of certainty. Perhaps the most striking of these is that the rates of diffusion of the six solute metals approach an identical value at low concentrations of solute, Fig. 15. Furthermore, the Q values appear similarly to approach a common value (Fig. 14), so that the D values may perhaps be taken as equal at all temperatures for these six solutes.

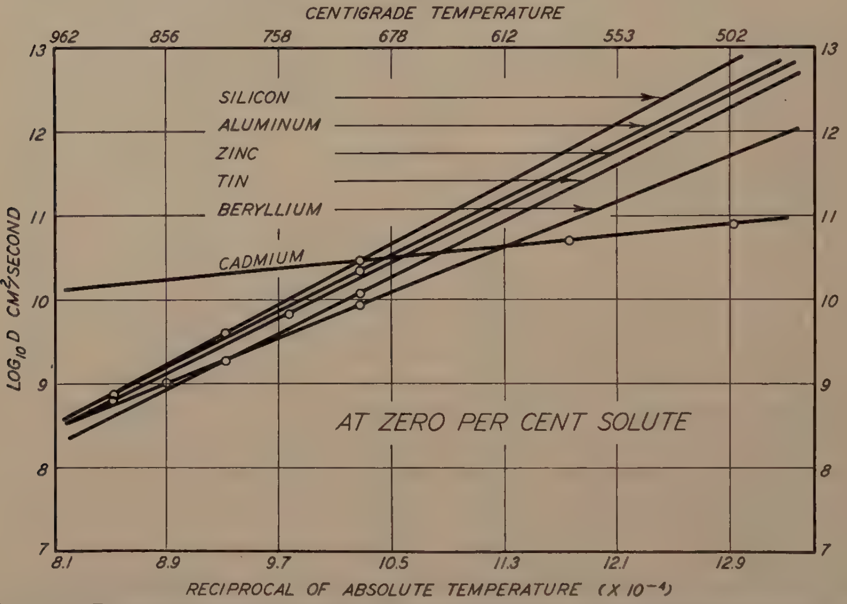

FIG. 16.—PLOT OF $\log_{10} D$ VERSUS $1/T$ EXTRAPOLATED TO ZERO CONCENTRATION OF SOLUTES FOR SYSTEMS CU-AL, CU-BE, CU-CD, CU-SI, CU-SN AND CU-ZN.

This is surprising, for there is no suggestion of such a behavior in other groups of systems. Although the effect of varying concentration on D was not determined on the system of lead* and of silver,* it hardly seems likely that these systems would yield the same result on proper analysis, since the D values in the individual systems differ so greatly. The data for the systems Au-Pt, Au-Pd, Au-Ni furnish the variation of D with concentration, but in this case the limiting D values in gold vary markedly while, surprisingly, the limiting D values in platinum, palladium, and nickel, respectively, do approach a common value; that is, the behavior appears to be the opposite to that noted in this work. There is thus no precedent for the data given here.

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* Seith: references 1, 7, 8.

Since the D values represent the rate of exchange of both solute and solvent atoms at a given concentration, it is possible that the observed rate is determined by the rate of exchange of the inherently slower, less mobile atom. As the concentration of the solute becomes less, the lattice more nearly approaches the lattice of copper in its physical properties, and the rate of diffusion of copper in very dilute solutions must thus be not greatly different from that of the rate of self-diffusion of copper. The rates of self-diffusion generally are low, and we may presume that the slower rate of diffusion in the dilute alloys, the rate that determines the observed D values, is the rate of self-diffusion of copper; in other words, that the common limiting D value to which all curves extrapolate is in fact the self-diffusion coefficient of copper. No separate determinations of the rate of self-diffusion of copper are available, so that this reasoning cannot be confirmed. The behavior of the systems of gold, which seems at first to be in opposition, may possibly be in confirmation: the rate of self-diffusion of gold should be higher than that of platinum, palladium or nickel, owing to the relative melting points, and the addition of platinum, palladium, or nickel to gold thus intrudes into the gold lattice an atom inherently less mobile, so that the rate of diffusion of these solutes and not the rate of diffusion of gold should control the D values in alloys limiting on gold, whereas in alloys limiting in concentration on platinum, palladium and nickel the controlling rate should be the rate of diffusion of platinum, palladium or nickel. Thus, if the rates of self-diffusion of platinum, palladium and nickel do not differ greatly at the temperature at which Jedele made his measurements (900° C.), the behavior of these systems is in accordance with the idea that in dilute solutions the observed D values approximate the rate of self-diffusion of the solute when this rate is slower than any other rate in the system.

Fig. 15 shows that the D values in all six systems increase with increasing concentration of solute, at first very slowly, and later very rapidly.* Attempts to associate the relative values of D at equal atomic concentrations with the several factors that have heretofore been advanced to explain the rate of diffusion in systems with a common solvent—namely, relative melting point, relative atomic radii for a common coordination number, degrees of solid solubility, types of space lattice, and relative positions in the periodic table (the electrovalent effect)—have been entirely fruitless. Although there are observable trends, in every case some solutes are exceptional. Furthermore, since the Q values in these six systems are not identical—and, in fact, may either increase or decrease with changing concentrations—the diffusion coefficients of the six solutes will appear in different relative order as temperature and concentration are changed, so that a fixed order of increasing rates of diffusion for the six solutes cannot be established. Thus, the D values of zinc and aluminum are nearly identical at 800° C. (Fig. 15), but since Q for the Cu-Zn system is less than that for the Cu-Al system, at temperatures above 800° C. the rate of diffusion of aluminum is greater than that of zinc, and below 800° C. less. The suggestion of Seith[13] that the D values at different concentrations might reduce to identical values if taken at equal fractions of the absolute melting point, is not confirmed by the present data. Whether all of the D curves should extrapolate to identical values at the maximum solid solubility cannot be said, though the idea is interesting. The curves rise rapidly at high concentrations, but the data become quite uncertain near the limit of the concentrations studied, as shown above, therefore it would be difficult to investigate the point.

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* Attempts to find a common mathematical form for these curves were unsuccessful.

The Q values for the six systems are surprising. The possibility that the Q values in dilute solutions may be equal suggests again that the rate of self-diffusion in copper is the controlling process. But it will be noted that though the D values invariably increase with concentration, the Q values sometimes increase, as in the Cu-Al system, and sometimes decrease, as in the Cu-Zn system. It has generally been assumed that high Q values require low D values, that if the potential barrier that an atom must surmount before it can move to another position becomes greater, a smaller fraction of atoms will be able to move and thus D will be smaller; the present results are not in conformity with this idea. The dynamics of atomic interchange in solid solution lattices is highly complicated, and the assumed relationship between D and Q probably represents an oversimplification in theory.

The data are not good enough to furnish information on the constancy of Q with temperature; there is reason to suspect minor variations from constancy, but data on metallic systems, limited to narrow temperature ranges, give no evidence of this, and since the present data are not sufficiently accurate to offer evidence on this point, straight lines have been employed in the log D versus $1/T$ plots, Fig. 13.

The only previous data with which the present data may be compared are those for the α Cu-Zn alloys obtained by Dunn[6] and by Bugakov and Rybaklo.[12] In both investigations the method adopted was that of vaporization of zinc into a vacuum and the calculation of the diffusion coefficient from the rate of loss of zinc. Dunn worked with two alloys containing 29.08 and 9.58 per cent Zn, respectively; he found D to be greater in the alloy with the higher zinc content, and in this respect his results are in agreement with the present results, though his values of D are necessarily averages over the concentration ranges between the alloy composition and pure copper; his value for Q is 42,000 cal., when calculated properly,[1] independent of the concentration of zinc, which is somewhat high compared to the present results. Bugakov and Rybalko used a single alloy composition with 30 per cent Zn, studying particularly the effect of grain size on the measured rate of diffusion, and finding that D increased with decreasing grain size; this result is very questionable for reasons pointed out previously;[1] their value of Q is in the neighborhood of 20,000 cal., which is much lower than that determined by Dunn and the values found here; their results must also be considered only as averages over a wide concentration range. The values of the diffusion coefficient of zinc in α-brass at 800° C. as read from Dunn's curves are: for the 9.58 per cent zinc alloy, 1.6×10^{-12} sq. cm. per sec.; for the 29.08 per cent zinc alloy, 5.6×10^{-12} sq. cm. per sec. The values obtained by Bugakov and Rybalko for 800° C. vary with grain size between 5×10^{-7} sq. cm. per sec. for small grains to 2×10^{-8} sq. cm. per sec. for a single crystal. The values obtained in the present work lie between 5×10^{-10} sq. cm. per sec. at zero per cent Zn and $> 60 \times 10^{-10}$ sq. cm. per sec. for the 30 per cent alloy; thus the present results lie between the two previously reported sets of data. The vaporization technique has several serious disadvantages,* which probably account for the lack of agreement between the data of Dunn and those of Bugakov and Rybalko, and between these and the present data. The technique adopted here is the more trustworthy.

The Dushman-Langmuir equation[1] is of but limited usefulness in its application to the present data. Taking the rate of diffusion of the various solutes near 100 per cent Cu at 800° C. as 4×10^{-10}, the Q values may be calculated by this equation as 44,000 cal., which is rather far from the observed value of 39,000 cal., though it will be observed in Fig. 14 that the extrapolated Q values show rather considerable scatter. Chief interest lies in the application of the equation to cases where on one hand Q decreases with increasing concentration of solute, as in the Cu-Zn system, and on the other hand increases with concentration of solute, as in the Cu-Al system. At 20 atomic per cent Zn the calculated Q value is 38,500 cal., as compared with the observed 31,000 cal.; the equation thus predicts a decrease in Q with increasing concentration which is observed. At 16 atomic per cent Al, the calculated Q value is 39,000 cal. as compared with the observed 54,000 cal.; thus the equation predicts a decrease in Q with increasing concentration, but the observations show an increase.

The calculation of Q from data on minimum creep rates by Kanter[11] appears to be of considerable importance. Unfortunately, no data have been found from which Q can be calculated in this way for alloys comparable in composition to those studied here, but such a calculation on copper yields a value of 39,000 cal.,† which is in good agreement with the coefficient of self-diffusion of copper as approximated here, Fig. 14;

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* See ref. 1. The wide divergence in the results using the vaporization technique suggests that there may be some unknown influences capable of exerting extremely powerful effects on the rate of dezincification. A study of these might well produce results of commercial importance.

† Private communication from Mr. J. J. Kanter.

furthermore, data on copper alloys, for the most part two-phase alloys, suggest that increasing zinc lowers the Q value, as found here, and that aluminum raises it, also as found here. For a more precise comparison of the Q values obtained in these two ways, additional creep data on simple binary alpha solid solutions of copper are much to be desired. If it could be shown that the values are invariably identical, knowledge of the creep mechanism would be greatly increased.

In studying the factors that control the rate of precipitation from solid solutions, we must, then, consider that the rate of diffusion of the precipitating solute in the matrix alloy may vary during precipitation—as the matrix becomes progressively more dilute—through wide limits, and that the initial rates for alloys of differing composition may be associated with quite different rates of diffusion. In the systems studied here D invariably increases with increasing concentration, but in other systems the opposite might well be observed.

With Q values varying with composition, in some cases increasing with solute concentration, and in others decreasing, it must be noted that the rates of homogenization of inhomogeneous, cored or segregated, alloys will vary with temperature[1] in quite different fashion for different alloy systems and for different alloy compositions within the same system.

SUMMARY

1. Diffusion coefficients have been determined from concentration-penetration curves by the Matano method for a series of alpha solid solutions in the systems Cu-Al, Cu-Be, Cu-Cd, Cu-Si, Cu-Sn and Cu-Zn.
2. This method provides the diffusion coefficient as a function of concentration, and thus diffusion coefficient-concentration curves have been plotted. The temperature coefficient of the diffusion rate—the activation heat of diffusion—has been calculated and activation heat-concentration curves have been plotted.
3. The various sources of error in such measurements have been critically discussed.
4. The rate of diffusion in these systems increases with increasing concentration of solute, at first slowly, then with increasing rapidity. The increase is more rapid in systems of low solid solubility than in systems of high. The rates of diffusion near zero concentration of solute are approximately equal for all systems, suggesting that the value extrapolated to zero concentration of solute is the rate of self-diffusion in copper and that this slow rate is the controlling rate in dilute solid solutions in this series.
5. The data on Cu-Zn alloys are not in accordance with those obtained by other workers using the vaporization technique.
6. No explanation has been found for the relative rates of diffusion in the systems studied, and it is suggested that previous explanations applied

to other systems have suffered from a lack of consideration of the variation in the diffusion coefficient with concentration.

7. The calculations of the activation heat of diffusion yield less dependable data. The activation heat is found to fall with increase in concentration in some systems and to rise in others, though the latter result is not in accordance with the requirements of the Dushman-Langmuir equation. The activation heats at zero concentration of solute, obtained by extrapolation, are not far from a common value. The activation heat calculated for pure copper from the best data is in accordance with that calculated from the temperature dependence of minimum creep rates.

ACKNOWLEDGMENTS

The authors wish to express their indebtedness to Dr. A. J. Smith, Mr. S. L. Woo, Mr. D. E. Lehane, Mr. R. Ward, Mr. H. P. George, Mr. W. A. Johnson and Miss E. B. Pearsall, for their assistance in carrying out this research. Grateful acknowledgment is also made to the American Brass Co., the American Smelting and Refining Co., the Bridgeport Brass Co., the Chase Brass and Copper Co., the Federated Metals Co., the Revere Copper and Brass Co., and the Scovill Manufacturing Co. for many favors, including the analysis of the diffusion samples.

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DISCUSSION

(O. E. Harder presiding)

P. A. BECK,* Perth Amboy, N. J. (written discussion).—An interesting result of this extremely important fundamental work by Dr. Mehl and Dr. Rhines is the exact demonstration of the considerable increase in the rate of diffusion of various solute atoms with their respective concentrations. The rate of diffusion of the solute atoms is changed in the same sense, by increasing their concentration, as it is changed by increasing temperature.

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* Central Research Laboratory, American Smelting and Refining Co.

A recent investigation of A. J. Phillips on the creep of lead and lead alloys[14] indicates that alloying elements, which are present in the form of solid solutions, decrease the creep resistance of lead. The rate of creep is increased, that is changed in the same sense, by the presence of solute atoms in the lattice, as it is changed by increased temperature.

It is well known that the temperature of recrystallization of solid solutions is higher than that of the pure metals. It is also known that if the temperature of cold-working is raised, the temperature that is required to produce recrystallization on subsequent annealing also increases. Here again the temperature of recrystallization is changed in the same sense, due to solid solution, as it is changed by increased temperature of deformation.

In work relating to the effect of third elements on the aging of lead-antimony alloys, Schumacher, Bouton and Ferguson[15] show that certain third elements, in small concentrations, have a pronounced accelerating effect on the rate of aging. It is interesting to observe that the most effective concentrations of these additions are in the neighborhood of their (rather low) solubility limits, where, according to the present paper by Mehl and Rhines, they may be expected to have the highest rate of diffusion. The change in the rate of aging, due to dissolved third elements, is again in the same sense as the change in the rate of aging due to increased aging temperature.

Even though these analogies may be only qualitative, and the available material is certainly not enough for broad generalizations, one is led to tentatively consider the question whether or not the similarity of the effects produced by solid solution in these various properties occurs because the underlying physical phenomena are closely related. Is the rate of diffusion of the solvent atoms themselves (the self-diffusion of the solvent metal) also increased by solid solution? Can this account for the increased creep rate at temperatures near or above the lowest temperature of recrystallization? Is the increased temperature of recrystallization due to a higher degree of recovery during annealing, before recrystallization has a chance to set in? Can the faster recovery, in turn, be explained by the increased rate of creep in localized submicroscopic areas? Finally, is the rate of diffusion of dissolved third elements also increased, thus accounting for the effect discovered by Schumacher and collaborators?

F. N. Rhines and R. F. Mehl (written discussion).—Doubtless the phenomena cited by Mr. Beck are related in some fundamental way, but the exact correlation among them may be complicated and certainly will require a great deal more work before the correlation will become evident. Recent work in the Metals Research Laboratory has indicated that the curve of recrystallization temperature for 50 per cent reduction in height by cold-rolling vs. concentration of zinc is of the same shape as the curve of the activation heat of diffusion vs. zinc concentration plotted in Fig. 14.

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[14] A. J. Phillips: *Proc.* Amer. Soc. Test. Mat. (1936) **36,** pt. 2, 170.

[15] E. E. Schumacher, G. M. Bouton and L. Ferguson: *Ind. and Eng. Chem.* (1929) **21,** 1042.

Age-hardening of Aluminum Alloys, III—Double Aging Peaks

By William L. Fink,* Associate Member, and Dana W. Smith,* Junior Member A.I.M.E.

(Atlantic City Meeting, October, 1937)

In parts I[1] and II[2] of this series, there were presented results of investigations on the age-hardening of an aluminum-copper and an aluminum-magnesium alloy. It was shown that the simple precipitation theory of hardening[3] adequately explained the aging phenomena, including certain so-called "anomalous" behaviors which had caused other investigators to reject or modify the precipitation theory. However, these papers did not discuss the double aging peaks, which have been stressed in recent articles by Dr. M. Cohen[4] and Dr. M. L. V. Gayler.[5] The present paper is devoted to an explanation of this "anomaly."

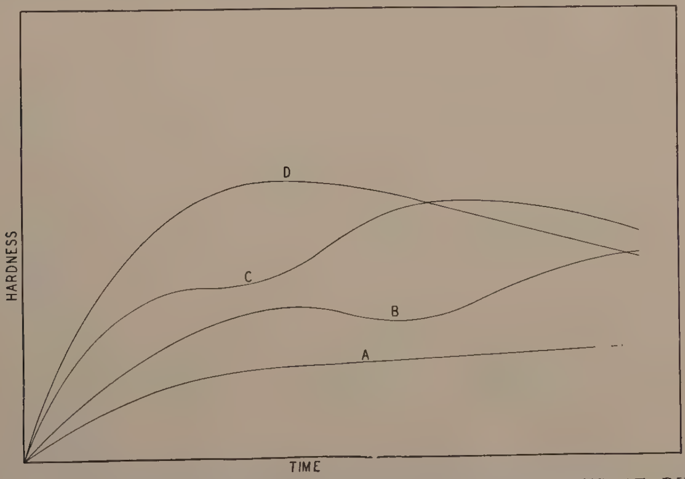

Fig. 1.—Schematic representation of age-hardening curves at different temperatures.

Fig. 1 is a generalized schematic representation of aging curves at different temperatures. Curve *A* corresponds to the aging at the lowest temperature, and *D* at the highest temperature. Certain previous investigators have explained curve *A* and the initial peaks

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Manuscript received at the office of the Institute Aug. 19, 1937.

* Aluminum Research Laboratories, New Kensington, Pa.

[1] References are at the end of the paper.

in curves *B* and *C* as due to pre-precipitation phenomena. The final peaks in curves *B* and *C* are assumed by them to be caused by precipitation. Curve *D* does not show any inflections, since precipitation is assumed to be essentially simultaneous with pre-precipitation phenomena. It seemed to the authors that these curves could be explained more simply and more satisfactorily on the basis of the theory of precipitation-hardening.

It has been known for some time that quenching in cold water produces plastic deformation. It has also been known that plastic deformation accelerates the rate of precipitation. If the plastic deformation occurs locally at grain boundaries and along slip planes, as would be expected, precipitation would occur at different rates in different parts of a given grain. This would adequately account for a hardness curve with two peaks. In Fig. 2 curve *A* would represent the course of precipitation hardening in those portions of a specimen which suffered plastic deformation. Curve *B* would represent the hardening in the portions that have not suffered plastic deformation. Ordinary macroscopic methods of measuring hardness, therefore, would yield an integrated curve such as curve *C*. Assuming this explanation to be true, it should be possible to change the magnitude of the first aging peak by changing the amount of plastic deformation; as, for example, by changing the rate of quench. In order to test this hypothesis, a series of experiments was performed on aluminum-copper alloys.

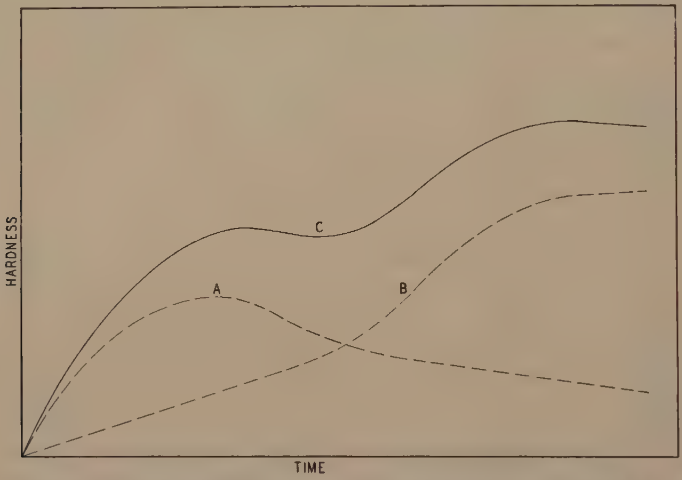


FIG. 2.—SCHEMATIC REPRESENTATION OF AN AGE-HARDENING CURVE AT AN INTERMEDIATE AGING TEMPERATURE.

A, precipitation-hardening in regions that have suffered plastic deformation during quenching.

B, precipitation-hardening in portions that have not suffered plastic deformation.

C, integrated curve of *A* and *B*.

MATERIAL AND PREPARATION OF ALLOYS

The aluminum used in the preparation of these alloys contained less than 0.01 per cent each of iron, silicon and copper. High-purity cathode copper was used.

For this investigation, there were prepared two lots of a binary aluminum-copper alloy containing approximately 4 per cent copper. Some of the 5.17 per cent copper alloy used in a previous investigation[1] was also used. The aluminum was melted in a plumbago crucible in an electric furnace, and the copper added. The melt was thoroughly stirred with a graphite rod and fluxed with chlorine gas before casting. The metal was cast as sheet ingots in a cold iron tilting mold (approximately 200 by 165 by 40 mm.) and into small chill-cast slabs for chemical analysis (75 by 40 by 5 mm.).

The chemical analyses were made upon drillings from the analysis slab. The analytical methods used were those described in "Chemical Analysis of Aluminum," published by Aluminum Company of America. The compositions of the alloys were found to be:

	Si	Fe	Cu
S-20817	0.01	0.01	4.00
S-26970	0.01−	0.01−	4.22

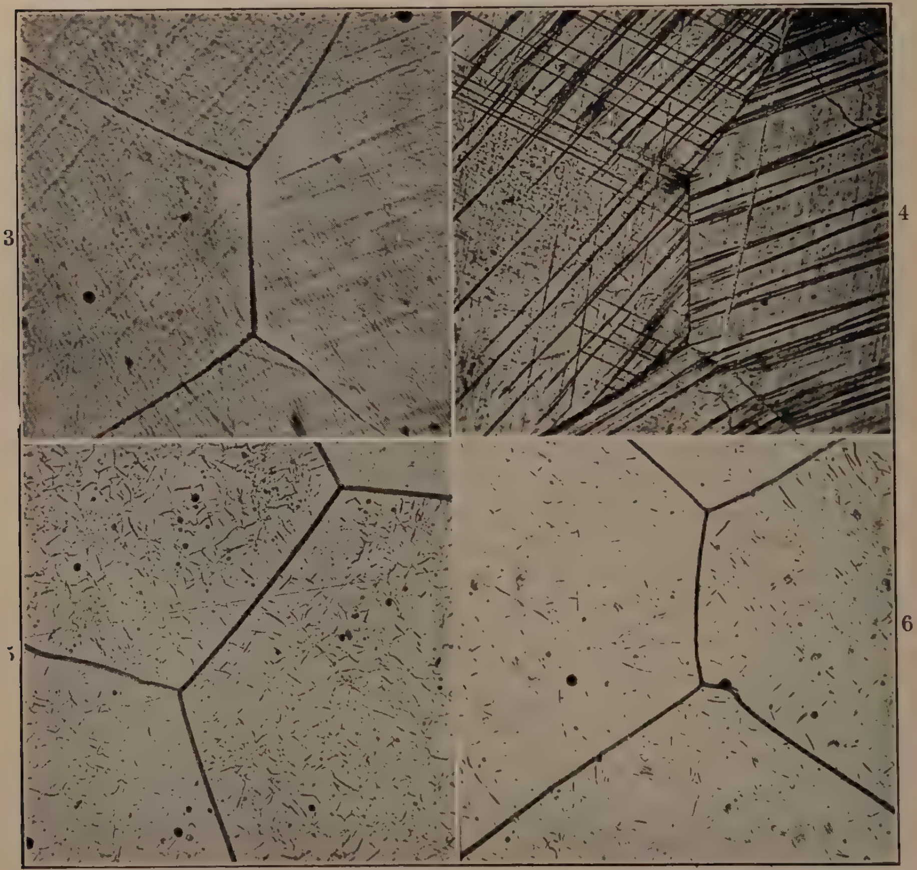
In order to insure homogeneity, the material received two heatings at 495° C. for a total time of 14 hr. during the hot-rolling of the ingot to a thickness of 6.4 mm. The sheet was then cold-rolled to a thickness of 1.6 mm. and cross-grain A.S.T.M. tensile specimens were machined with a formed milling cutter. All of the specimens were heated for 16 hr. at 525° C. prior to quenching and aging. Some of the samples were quenched in water at approximately 25° C. and subsequently aged at room temperature, 100° or 153° C. Other specimens were quenched directly into the oil aging bath at either 100° or 153° C. The aging bath was an oil thermostat, the temperature of which was controlled within ±0.05° C.

MICROSCOPIC EXAMINATION

Initial investigations concerning the nature of plastic deformation during quenching and its effect on the microstructure of subsequently aged samples were carried out using the binary aluminum-copper alloy containing 5.17 per cent copper. Duplicate investigations using the 4 per cent copper alloys gave exactly similar results.

The water-quenched samples were first examined to verify the hypothesis that plastic deformation occurred locally at grain boundaries and along slip planes. This was done by polishing the sample before quenching and examining it after quenching without repolishing. Fig. 3

is typical of the observed structures which amply verified the hypothesis. The grain boundaries and slip planes are clearly revealed by the relief produced by plastic deformation. The slip bands, which do not cross the grain boundaries, can be readily distinguished from scratches on the polished surface, which do cross grain boundaries. After aging at 200° C. for 2 hr., this specimen was repolished and microscopically examined to verify the hypothesis that precipitation occurred more rapidly in the deformed regions. Fig. 4 shows the same area after aging and repolishing. There is an obvious coincidence of the loci of the precipitate and the slip bands and grain boundaries. This experiment was repeated many times with the same results.



Figs. 3–6.—Aluminum-copper alloy (5.17 per cent Cu) heated 16 hours at 540° C. × 100.

Fig. 3. Polished, as-quenched in water at 25° C.

Fig. 4. Same as Fig. 3 after being aged 2 hr. at 200° C., lightly polished and etched.[1]*

Fig. 5. Quenched in boiling water, aged 2 hr. at 200° C., polished and etched.*

Fig. 6. Quenched in oil at 153° C., aged 2 hr. at 200° C., polished and etched.*

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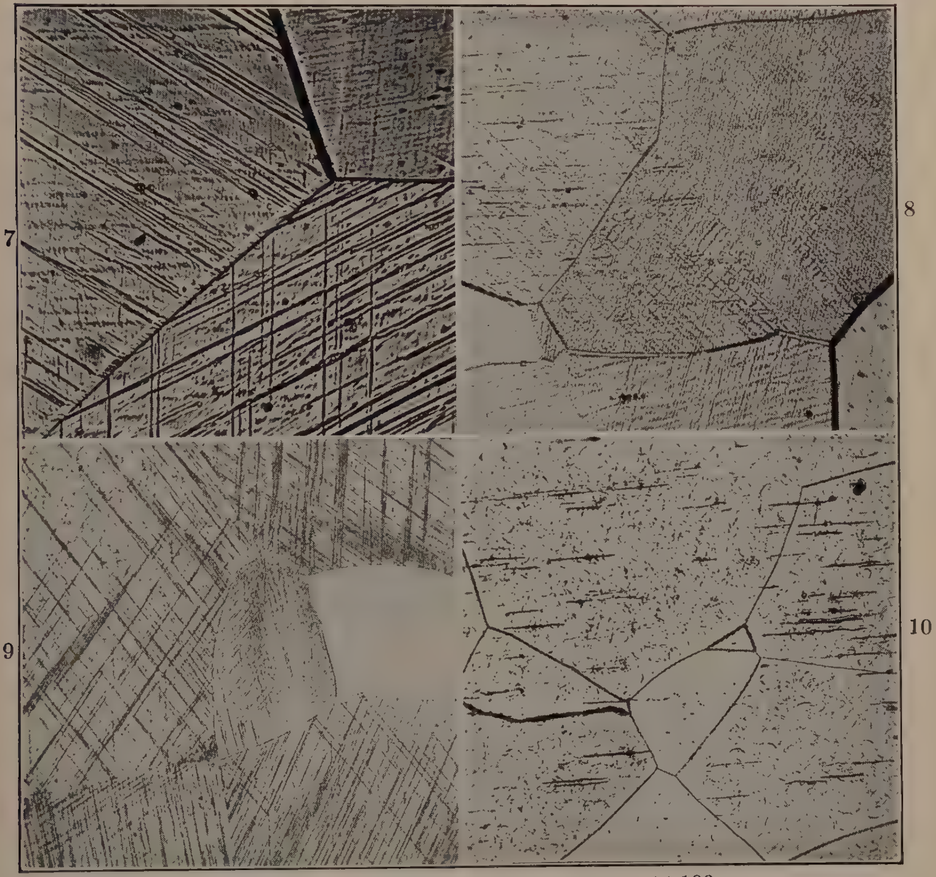
* See note on page 233 regarding etching procedure.

The experiment was repeated using specimens quenched in boiling water and oil at 153° C. No evidence of slip could be detected on the polished as-quenched samples, and subsequent aging at 200° C. for 2 hr. revealed that general precipitation had taken place without any tendency to concentrate upon slip planes. Figs. 5 and 6 illustrate the structures obtained in samples quenched in hot water and oil and subsequently aged. While there does appear to be some directionality of the precipitate, varying from grain to grain, this is probably of a Widmanstätten nature.



Figs. 7–10.—Aluminum-copper alloys. × 100.

Fig. 7. 4.00 per cent Cu, heated 16 hr. at 525° C., quenched in water at 25° C. and aged 5 min. at 100° C., polished and etched.

Fig. 8. 4.22 per cent Cu, heated 16 hr. at 525° C., quenched in water at 25° C. and aged 2 min. at 153° C., polished and etched.

Fig. 9. Same as Fig. 8 but aged 216 hr. at 153° C., polished and etched.

Fig. 10. 4.22 per cent Cu, heated 16 hr. at 525° C., quenched in oil at 153° C. and aged 216 hr. at the same temperature, polished and etched.

Evidences of precipitation in the samples of 4 per cent copper alloys that had been quenched in water at room temperature and subsequently aged at 100° and 153° C. were definitely shown even after the shortest periods of aging at each temperature. In these a readily detectable "pattern" is formed by precipitation along slip bands. Fig. 7 is representative of a water-quenched sample of the 4.00 per cent copper alloy aged 5 min. at 100° C. while Fig. 8 is of a water-quenched sample of the 4.22 per cent copper alloy aged 2 min. at 153° C. Continued aging up to 384 hr. at 100° C. did not appreciably change the microstructure of the 4.00 per cent copper alloy. The 4.22 per cent copper alloy after aging 216 hr. at 153° C. showed a considerable increase in precipitate particle size (Fig. 9).

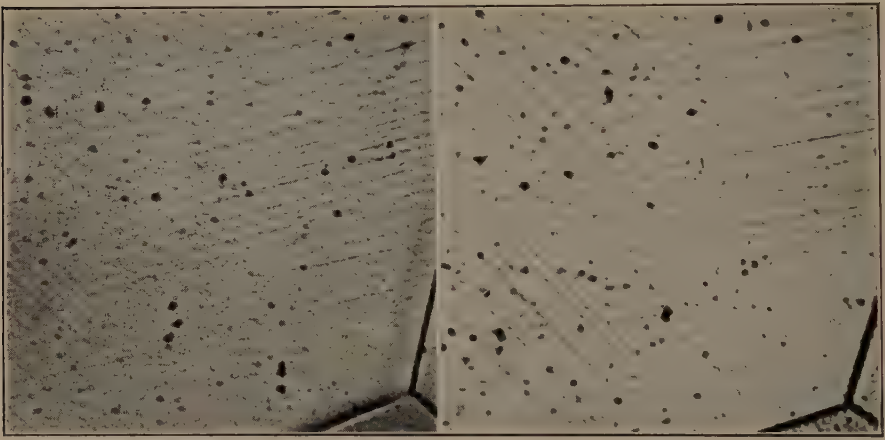


Fig. 11. Fig. 12.

Figs. 11–12.—Aluminum-copper alloys. × 100.

Fig. 11. 5.17 per cent Cu, heated 16 hr. at 540° C., quenched in water at 25° C. and aged 1¼ hr. at room temperature.

Fig. 12. Same as Fig. 11 but aged 6½ hr. at room temperature.

Since, as previously pointed out, slow quenches produce much less plastic deformation in the alloy samples, it is more difficult to detect evidences of initial precipitation in these samples because of the lack of a readily detectable pattern. In the samples quenched in oil at 100° C. and aged at the same temperature, precipitation could not be definitely revealed even after 384 hr. Precipitation could be definitely shown in those samples quenched in oil at 153° C. after an aging time of 8 hr. at the same temperature. After 216 hr. at this temperature precipitation is very clearly shown, as in Fig. 10.

In Part I[1] no detailed investigation was made of precipitation at room temperature. An incidental observation that precipitation could be seen after three months at room temperature was reported. In the present investigation, much shorter aging times at room temperature were employed. The shortest period at which precipitation was observed in water-quenched samples of both the 4.00 and the 5.17 per cent copper alloys was 1¼ hr. Only a few grains showed precipitation in this short interval. One such area in a 5.17 per cent copper alloy sample is shown in Fig. 11. Repeated examination at various intervals showed increased precipitation. Fig. 12 shows the same area as Fig. 11 but after 6½ hr. aging. Additional aging resulted in more grains showing precipitation. After 31 hr. practically all of the grains showed precipitation. The change in microstructure between 31 hr. and 3 months (previously reported) was not marked.

Mechanical Tests

The progress of the precipitation-hardening was followed by determining tensile strength, yield strength, elongation and hardness. The tensile tests were made in an Amsler testing machine equipped with self-aligning grips.[6] The yield strength was determined from the stress-strain curve drawn by an electric recording extensometer.[7] The hardness was determined with a Rockwell hardness tester using a load of 100 kg. and a ⅛-in. ball (scale E). The results of the mechanical property tests are given in Figs. 13 to 17.

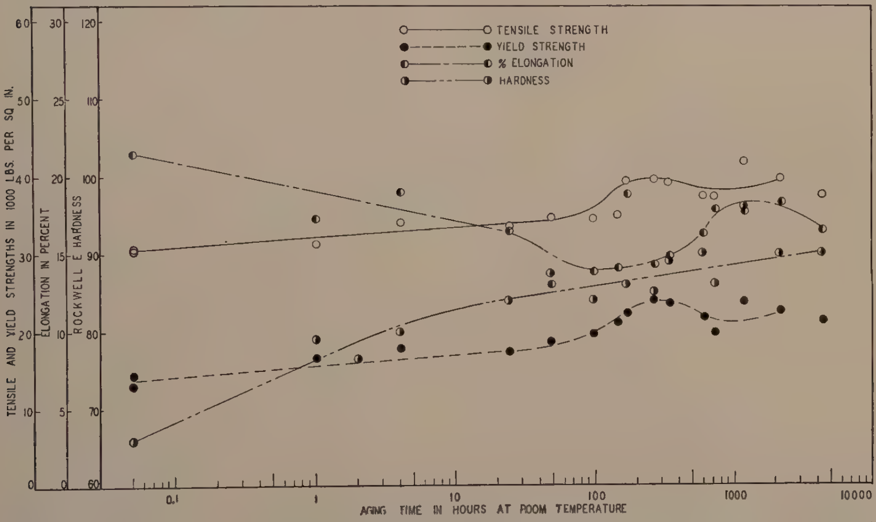


Fig. 13.—Plot of age-hardening data of Al-Cu alloy (4.00 per cent Cu) quenched in water at 25° C.

Discussion of Results

In Figs. 13, 14 and 16 are plotted the aging curves for the water-quenched samples aged at room temperature, 100° and 153° C., respectively. These curves show initial peaks followed by softening, and then the principal aging peak. The initial aging peaks and subsequent softening are best shown in the tensile and yield-strength

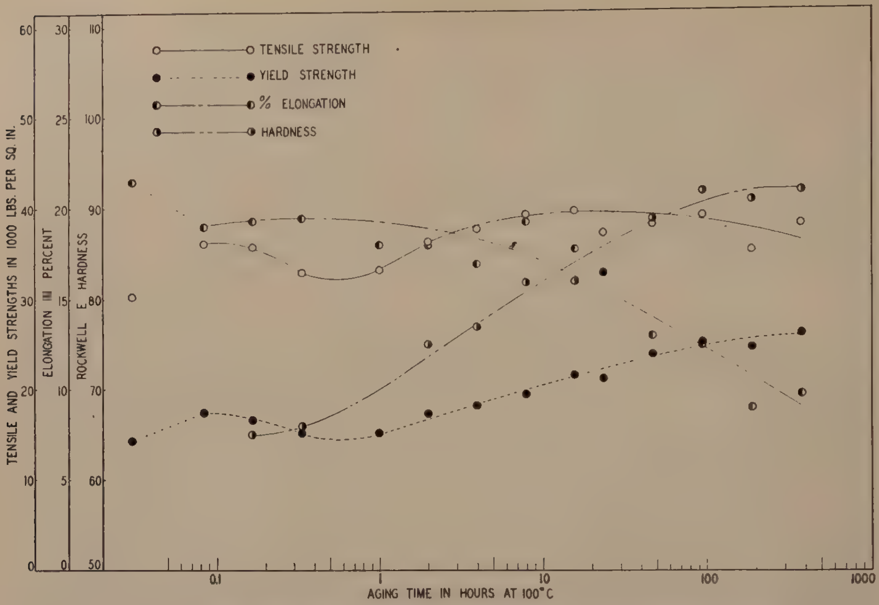


FIG. 14.—PLOT OF AGE-HARDENING DATA OF AN ALUMINUM-COPPER ALLOY (4.00 PER CENT CU) QUENCHED IN WATER AT 25° C.

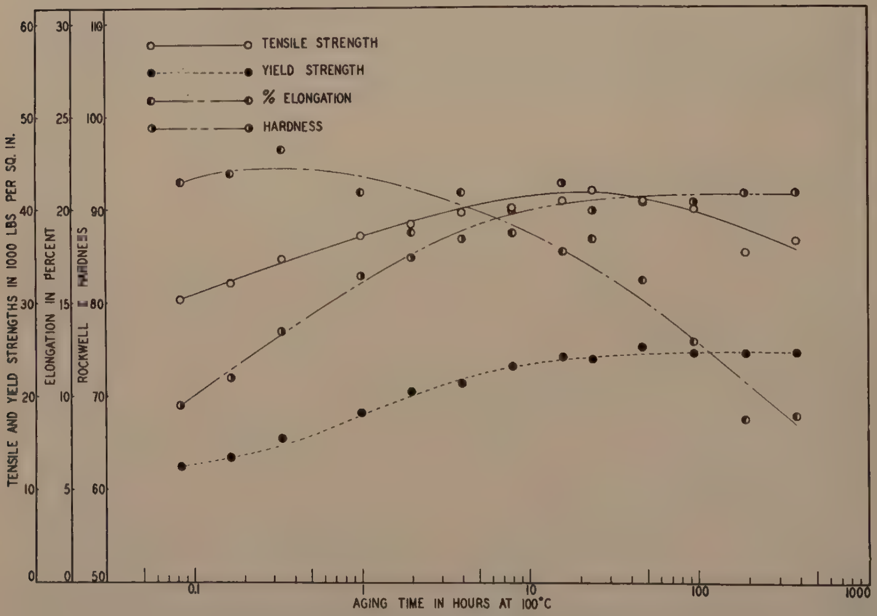


FIG. 15.—PLOT OF AGE-HARDENING DATA OF AN ALUMINUM-COPPER ALLOY (4.00 PER CENT CU) QUENCHED IN OIL AT 100° C.

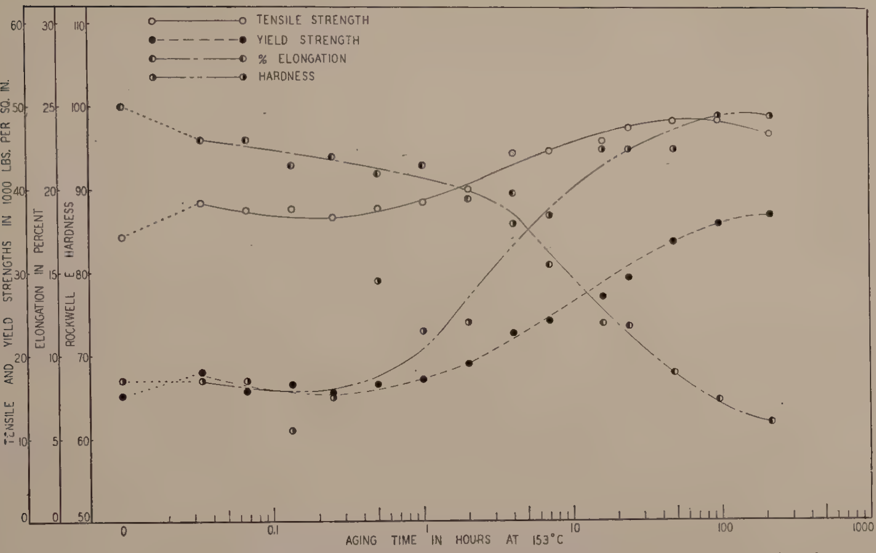


FIG. 16.—PLOT OF AGE-HARDENING DATA OF AN ALUMINUM-COPPER ALLOY (4.22 PER CENT CU) QUENCHED IN WATER AT 25° C.

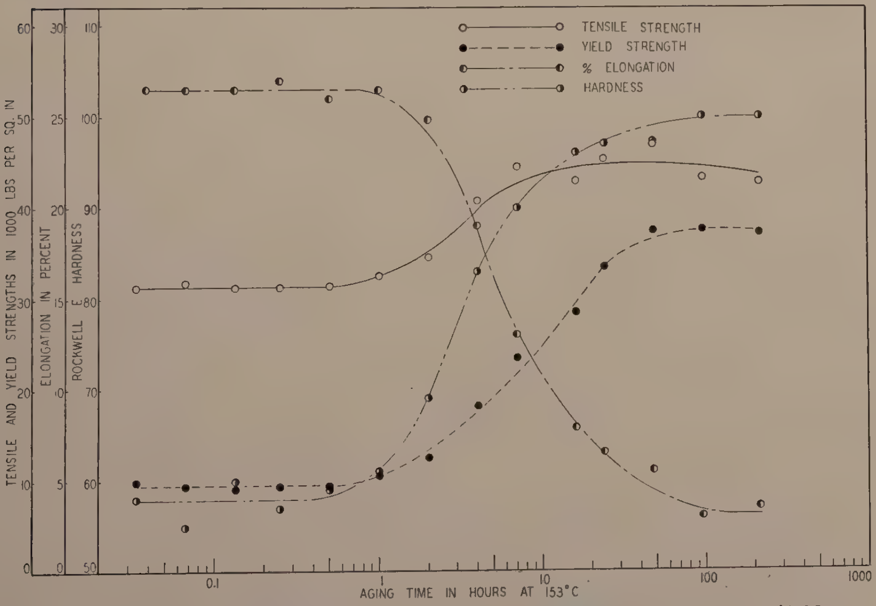


FIG. 17.—PLOT OF AGE-HARDENING DATA OF AN ALUMINUM-COPPER ALLOY (4.22 PER CENT CU) QUENCHED IN OIL AT 153° C.

curves, hardness measurements apparently being less sensitive to these early stages of hardening. Elongation also follows the same general course as do the tensile and yield strength, although, of course, they are affected in opposite directions. It is apparent from these curves that the time required to reach the first aging peak varies with the aging temperature. For example, aging at room temperature requires 264 hr. to reach the first peak while at 100° C. it is reached in 0.083 hr. (5 min.) and at 153° C. less than 0.03 hr. (2 min.) is required.

For the materials quenched in hot oil (Figs. 15 and 17), no initial aging peaks are observed. The hardening progresses continuously in a manner similar to the latter part of the aging curves of the water-quenched materials. The series of samples quenched and aged in oil at 153° C. did not start to show any hardening until after approximately 1 hr., while the series quenched and aged in oil at 100° C. started to harden almost immediately. Since it is well established that a higher aging temperature will cause more rapid hardening, it would be expected that this difference in age-hardening between these two series would be reversed if both series had received the same quench. It is concluded that the material quenched and aged in oil at 153° C. started to harden later than that quenched and aged in oil at 100° C., because it suffered the least from plastic deformation during quenching and therefore benefited the least from the accelerating effect of deformation on precipitation.

Comparing the results of the mechanical tests and microscopic examinations, it was evident that where double aging peaks are detected the microstructures showed preferential precipitation along slip bands. Where the hardening curves showed a single peak, corresponding to the second in the double-peak curves, in the first place, it was difficult to detect evidences of precipitation; and, secondly, when they were observable the precipitate was generally distributed with no tendency for preferential location on slip planes. In other words, the first peak in the aging curves of these alloys can be explained simply by the more rapid precipitation in the regions that have experienced plastic deformation during quenching. The softening that follows the first hardening may be due to overaging in these same regions. Further hardening is accompanied by more general precipitation.

It is suggested that the same mechanism accounts for the double peaks observed in the age-hardening curves of other high-purity binary alloys.

ACKNOWLEDGMENTS

The authors express their appreciation to Messrs. G. W. Wilcox and C. W. Cline, who prepared the specimens for microscopic examination; to Mr. H. V. Churchill, under whose direction the chemical analyses

were made; and to Mr. R. L. Templin, under whose direction the mechanical property tests were made.

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4. M. Cohen: *Trans.* A.I.M.E. (1937) **124,** 138.
5. M. L. V. Gayler: *Jnl.* Inst. Metals (1937) **4,** 55.
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7. R. L. Templin: *Proc.* Amer. Soc. Test. Mat. (1932) **32,** II, 783.

ETCHING PROCEDURE

The etching procedure was developed by Mr. F. Keller of the Aluminum Research Laboratories. It consists in first immersing the specimen in a 25 per cent solution of nitric acid at 70° C., washing in water, then immersing it in a solution containing 0.5 gram of sodium fluoride, 1 c.c. of nitric acid (conc.), 2 c.c. of hydrochloric acid (conc.) per 100 c.c. of solution. The time required in each solution and the number of times the etching procedure was used varies with the aging treatments the samples received.

DISCUSSION

(Albert J. Phillips presiding)

M. COHEN,* Cambridge, Mass. (written discussion).—I am very glad to see this convincing demonstration of the existence of double peaks in the aging curves of high-purity aluminum-copper alloys. Double hardness peaks in commercial aluminum-copper alloys have been regarded somewhat skeptically, and it has been common to find the minor peak attributed to the precipitation of some impurity or compound thereof. By preparing very pure alloys, the authors have eliminated this possibility. They are further to be congratulated because it is obvious that these double peaks can be revealed only by numerous careful and accurate measurements. For this very reason, it is quite possible that the reinvestigation of many of the common age-hardenable alloys, both pure and commercial, would disclose a more general occurrence of these double peaks.

However, I must disagree with the authors on their explanation of the cause of these peaks. Certainly the occurrence of plastic deformation during quenching must have a pronounced effect on the subsequent aging, but it seems unlikely that this plastic deformation is generally responsible for the initial peaks in this and other age-hardenable systems. It is quite possible that the initial hardness peak is due to pre-precipitation phenomena, but that the slow quenching permits submicroscopic precipitation to occur in some regions, which overlaps the pre-precipitation effects and hence masks out the initial peak. Therefore, it does not necessarily follow that the disappearance of the initial peak with slower quenching is due to the absence of plastic deformation. I would suggest that quenching from a lower temperature (at which the alloy is stronger and therefore more able to resist plastic deformation) would be a more satisfactory method for avoiding plastic deformation during quenching than to quench at a slow rate. Then the possibility of premature precipitation would be eliminated as a variable.

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* Division of Physical Metallurgy, Massachusetts Institute of Technology.

The possibility of premature precipitation taking place during slow cooling also explains the anomaly noted by the authors on page 232; namely, that the initial rate of aging of the sample quenched and aged in oil at 100° C. is greater than that of the one quenched and aged in oil at 153° C. The slower rate of cooling should permit more premature precipitation, and the lower degree of supersaturation effected thereby may account for the slower rate of aging even at the higher temperature.

According to the explanation offered by the authors, it is assumed that the intermediate softening between the double peaks is due to the overaging of the plastically deformed regions before the corresponding softening effect can be counterbalanced by the precipitation in the areas that have not been plastically deformed. This means that many of the precipitated particles in water-quenched samples would coalesce beyond the critical size for maximum hardening by the time the bulk of the precipitate in the non-deformed regions reaches the critical size distribution that causes the secondary peak. Hence, if the authors' theory is correct, water-quenching should decrease the maximum hardness and strength attainable by aging because it promotes nonuniformity of precipitation, and thereby fewer particles simultaneously reach the critical size for maximum hardening. Yet the comparison made in Table 1 shows that the rate of quenching has no consistent effect on the maximum values attained on aging.

TABLE 1.—*Maximum Yield Strength, Tensile Strength and Hardness Attained on Aging*[a]

Aging Temperature, Deg. C.	Quenching Medium	Maximum Yield Strength, Lb. per Sq. In.	Maximum Tensile Strength, Lb. per Sq. In.	Maximum Hardness
100	Water at 25° C.	26,000[b]	39,000	92
	Oil at 100° C.	25,000	42,000	92
153	Water at 25° C.	37,000	48,000	100
	Oil at 153° C.	38,000	45,000	100

[a] Values are only approximate, and are taken from the graphs in Figs. 14, 15, 16 and 17.

[b] Maximum value not quite attained.

Finally the postulation of accelerated precipitation due to plastic deformation cannot explain the contraction found during low-temperature aging by Portevin and Chevenard.[8] Precipitation of either the transition θ' phase or the denser stable θ ($CuAl_2$) phase should cause an expansion.

Therefore, while I believe that the authors have done an important piece of work in calling attention to the possible occurrence of plastic deformation during water-quenching, it still seems that the simple precipitation theory is not adequate to explain all the phenomena encountered in age-hardening.

G. SACHS,* Newark, N. J.—The authors have given an excellent set of experiments and some new facts on precipitation-hardening of aluminum alloys, but I do not feel that these facts have changed appreciably the present situation. Regarding myself, I am still definitely of the opinion that the simple precipitation theory is not able to explain the age-hardening phenomena. Under simple theory I understand that grain size, amount and distribution of distinct precipitated particles are the dominating factors according to the scheme developed some years ago by Jeffries and Archer.

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[8] A. Portevin and P. Chevenard: *Rev. de Mét.* (1930) **27**, 412.

* Baker & Co., Inc.

My first experiments with aluminum alloys were carried out mainly on single crystals made by the recrystallization method, as developed by Carpenter and Elam on pure aluminum. We found there the later much discussed double peak in the yield point and tensile strength; i.e., two maxima in these properties at different aging temperatures.

Also, our experiment showed that the crystal testpieces treated according to these distinguished conditions behaved extremely differently. A real single crystal changes its circular cross section in a tensile test to an elliptical cross section, because of gliding on one set of slip planes. That is exactly what happens with quenched crystals age-hardened at room temperature (first peak). What does it mean? It means, obviously, either that precipitated particles have no effect at all on the behavior of single crystals in tensile tests or that the amount of precipitated phase is so small that it does not affect the gliding mechanism. But, age-hardened at higher temperatures (second peak), the crystal testpieces behave quite differently. They behave like polycrystalline samples, in spite of the fact that the X-ray picture is the same as for a single crystal. The test pieces remain in a tensile test cylindrical. Precipitated particles of a certain amount hinder, therefore, the simple gliding mechanism of single crystals and force them to glide in many different directions like the crystals in polycrystalline material.

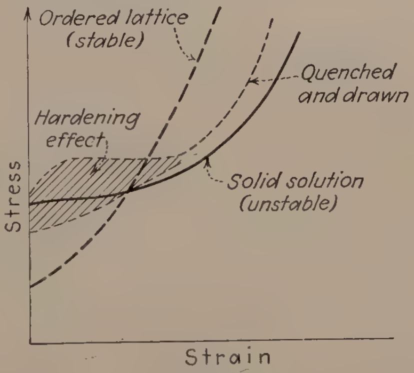

FIG. 18.

The conclusions from these experiments, as well as from many other observations, including the photomicrographs in this paper, are, therefore, that corresponding to the first hardening peak there is only a very small amount of precipitated particles present. This amount is probably not more than 0.1 per cent copper, or 1 per cent of the copper present in the alloy.

Now, the whole problem may be reduced to the following question: Why should 1 per cent of a precipitated phase give to an alloy about the same hardness as 100 per cent, whereas an alloy with only 1 per cent, i.e., 0.05 per cent copper (over the limit of solubility), does not age-harden at all?

Another interesting fact was confirmed by these experiments on single crystals. The cold-hardened crystals have a low yield point and a high elongation, the warm-hardened crystals a high yield point and a low elongation.

In connection with the theory of age-hardening in aluminum alloy, it may be interesting to mention some experiments on homogeneous gold-copper alloy crystals of the composition $AuCu_3$. This alloy exists in two "phases," in a solid solution with a "disordered lattice," stable only at high temperature, and in an "ordered lattice" stable at room temperature (Fig. 18). Both phases have clearly different properties. During the transformation from the high-temperature phase to the low-temperature phase, the atoms change their positions. When this is done at sufficiently low temperatures (quenched and drawn) there are small but quite definite hardening effects, as shown in the stress-strain diagram at tensile tests, Fig. 18. After prolonged heating, this "age-hardening" is again eliminated. A simple change of the atom positions in an alloy at sufficiently low temperatures causes, therefore, a certain hardening of the lattice. The slip planes may be regarded as "roughened" by the trail of the diffusing atoms.

I do not see how any precipitation process can be explained without some initial changes in the lattice. I do not see how the changes in hardness, electrical resistance, volume, etc., can be explained without the assumption that these changes of atom positions change the properties of the crystal lattice. Naturally, this process can be regarded also as a part of the precipitation process. That is only a matter of definition.

E. M. Wise,* Bayonne, N. J.—In these alloys simplicity was an object; that is, the nature of precipitate was as little complicated as possible. In commercial alloys such simplicity may not prevail. In some alloys there seems to be ample evidence of two or more separate and distinct precipitates involved, which will yield corresponding peaks in the aging curve. Examples are cited below.

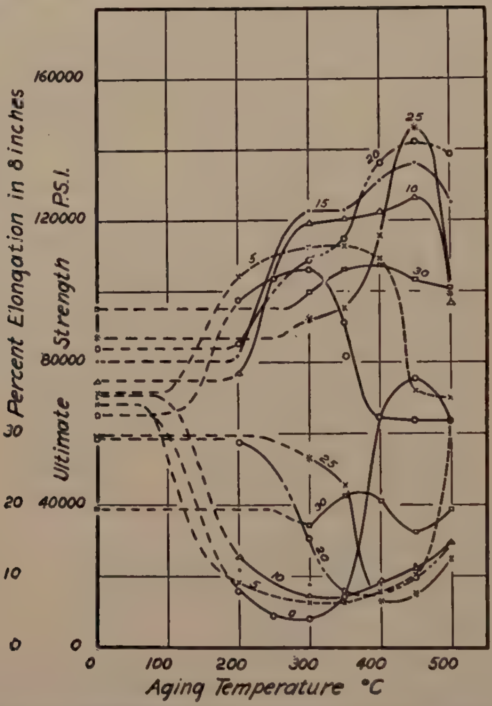

Fig. 19.—Effect of aging temperature and palladium content on properties of alloys initially quenched at 700° C.

From The Role of the Platinum Metals in Dental Alloys, II, by Walter S. Crowell, E. M. Wise and J. T. Eash. *Trans.* A.I.M.E. (1932) **99**, 392.

Fig. 19 shows the tensile strength of a group of dental alloys containing gold, palladium, silver and copper, in which about 29 per cent of copper was present and the amount of gold plus palladium was 50 atomic per cent, and which had been aged for 15 minutes at the indicated temperatures.

The curve of tensile strength against aging temperature for the 0 palladium alloy shows a single rather sharp peak at 300° C. The replacement of 5 atomic per cent gold by palladium broadens and raises the curve of strength vs. aging temperature, while 10 atomic per cent palladium causes a further shift toward higher aging temperatures and introduces a mild peak at 450° C. Increasing the palladium to 25 atomic per cent yields a narrow aging curve with a maximum at 450° C. These aging characteristics strongly suggest that two precipitation or ordering processes are involved, which proceed, with the aging time employed, at about 300° and 450° C., respectively, the intensity of the latter depending upon the palladium content and becoming the principal transformation in the 25 atomic per cent palladium alloy.

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* Metallurgist, International Nickel Co.

These deductions were later confirmed by X-ray studies of the phases present in aged alloys. The alloys containing no palladium changed from a face-centered cubic to a face-centered tetragonal upon aging while the 15 and 25 atomic per cent palladium alloys aged at 450° C. developed three phases: face-centered cubic, face-centered tetragonal and body-centered tetragonal in the former and two face-centered cubics and a body-centered tetragonal in the latter.[9]

A. J. Smith,* Cincinnati, Ohio.—Is there any way of estimating the amount of plastic deformation that is present in the various materials worked with here?

A few years ago I was bequeathed a single crystal of 5 per cent copper aluminum which had been used by Dr. Phillips and Dr. Brick in some work they had done about two years earlier. This was before their work on the influence of quenching stress on lattice-parameter measurements and in view of the later work the sample had probably taken a good deal of punishment, for it had been quenched in cold water a number of times from a solution heat-treatment and after quenching it had been allowed to precipitate almost completely at various—now unknown—temperatures. How many times this had been done I do not know, but after I received the crystal I performed the same operations at least three times.

With all of this drastic treatment there was no change in the orientation as measured X-ray-wise and I do not believe there was any change in its single-crystallinity. Apparently, then, the amount of plastic deformation resulting from such stressing was not sufficient to cause recrystallization.

R. H. Harrington,† Schenectady, N. Y.—I really should not attempt any critical attitude toward the data in this paper since I know so little about aluminum alloys.

I believe it would be of great value if the authors could give results of resistivity measurements on the alloy so treated in this paper so that their work could be adequately compared with that of Dr. Gayler in her last paper dealing with what she chose to call a "new theory of age-hardening." I believe that their explanation of their data does not conform with that from the data that she has published in that paper. As to which is at variance with the actualities, I do not know.

I believe it would be interesting to have the results of X-ray evidence to show definitely that a precipitate of definite compound in these slip planes has taken place, if that has occurred, and that this is distinctly a different situation from that formed from the viewpoint of Sachs and Gerber and Gayler, since in the first peak studied by them I believe it was definitely shown that no actual precipitation of a compound took place.

Then, I am afraid a great deal more work would have to be done before the general statement that this explanation would account for the double aging peaks in all other alloys would be acceptable.

We have a good deal of information on both ferrous and nonferrous alloys other than copper and aluminum or aluminum alloys in general. These data definitely fit in with the observations of Dr. Gayler and Dr. Sachs in their methods of accounting for the two aging peaks.

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[9] E. M. Wise and J. T. Eash: The Role of the Platinum Metals in Dental Alloys, III. *Trans.* A.I.M.E. (1933) **104,** 296.

* Lunkenheimer Co.

† General Electric Co.

G. Sachs.—I would like to make one point clear. The X-ray tool was never regarded as sensitive enough to prove the existence or absence of a small amount of a second phase. Therefore, it was really never assumed that in the cold-aged state precipitated particles are absolutely missing. It was only assumed that their amount is too small to explain the discussed effects.

D. W. Smith.—Dr. Fink and I appreciate greatly the interest shown by the discussion. It is to be hoped that interest in age-hardening will be maintained until all of the processes operative in this phenomenon are clearly explained to the satisfaction of those experienced in studies on this subject.

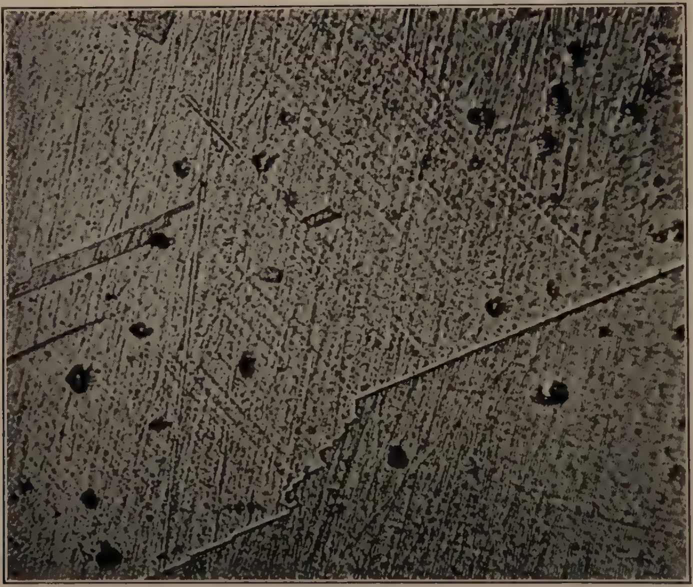

Fig. 20.

Dr. Cohen has suggested that premature precipitation, i.e., precipitation during quenching, in our aluminum-copper alloys might overlap pre-precipitation effects and hence mask out the initial peak. If that were true a higher hardness would be expected in the oil-quenched sample than in the water-quenched samples immediately after quenching. We noted no such general relation in our alloys, although there were indications of such precipitation in some of Dr. Cohen's samples of silver-copper alloy, which we studied.

Dr. Cohen very kindly supplied us with a few samples of a silver-copper alloy on which he reported last year at this time. We wished to see whether by any chance we could show the same general characteristics that we had observed in our aluminum-copper alloys.

Fig. 20 is a photomicrograph (500 ×) of one of the silver-copper alloy samples Dr. Cohen sent us. It had been heat-treated at 765° C. and quenched in cold water, then aged at 100° C. for 4 hr. Evidence of lined-up precipitation is apparent here just as in our aluminum-copper alloys. It must be admitted that it is not as clearly resolved as in our aluminum-copper alloys, but I have no doubt that had we spent the same length of time developing the polishing and etching techniques for this alloy as we have in developing them for our aluminum-copper alloys, we could have revealed the precipitation to better advantage than illustrated here.

Two other samples of the same material were heat-treated according to the practice recommended by Dr. Cohen. One was quenched in cold water and the other in oil at 150° C. Subsequent to these quenching treatments the materials were aged at 100° C.

Fig. 21 shows the hardening curves together with the hardening curve originally determined by Dr. Cohen. There is considerable variation between the three curves. In the first place, the initial "as-quenched" hardness values for the three samples are not identical. The differences indicate, as Dr. Cohen has suggested in his discussion, that precipitation during quenching may have occurred in this alloy and resulted in higher initial hardness in the more slowly quenched samples. During the first attempt to quench one of these samples in hot oil, delays were experienced in transferring it from the heat-treating furnace to the quenching bath. After this delayed quench, the initial hardness was 88 Rockwell F. This value was so far above the initial hardness value reported by Dr. Cohen that the heat-treatment and quenching of this sample was repeated. The transfer of the specimen from the furnace to the quenching bath during this second attempt was accomplished with greater rapidity and the initial hardness value was found to be 74 Rockwell F.

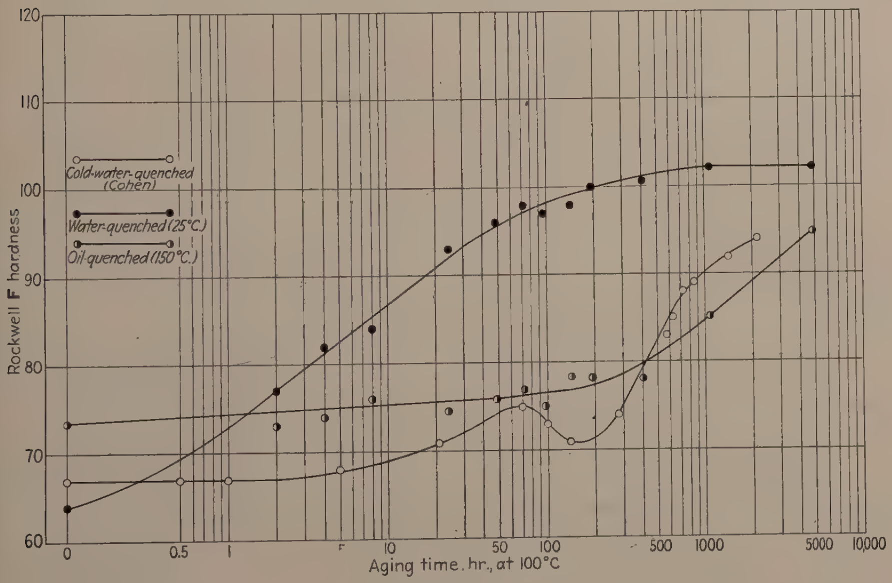

FIG. 21.

It is also to be noted that widely different rates of hardening, depending on quenching conditions, are indicated by the curves. Our water-quenched sample shows a rise in hardness very soon after the start of aging at 100° C. It also reaches its final maximum hardness sooner than was indicated by Dr. Cohen's investigations. On the other hand, our oil-quenched sample hardens very slowly and has not reached its maximum even after 5000 hr. at 100° C.

If the initial hardness values can be taken as criteria of the rate of quenching the three samples, it appears that our water-quenched sample obtained a faster quench and our oil-quenched sample a slower quench than was obtained with the material reported by Dr. Cohen. Under these circumstances, it may be reasoned that the greater amount of plastically deformed material, produced in our water-quenched sample by the more rapid quench, has accelerated the rate of hardening. Conversely, the absence of plastically deformed material in our hot-oil-quenched sample makes this material harden at an appreciably slower rate.

Dr. Cohen referred to the initial contraction observed during studies made by Portevin and Chevenard on aluminum-copper alloys. This contraction was not observed on high-purity binary aluminum-copper alloys but on an alloy containing substantial quantities of silicon. We hope in the very near future to have data concerning the dilation of the high-purity alloys that we used. It is hoped that at that time we will be able to tell whether or not there is an initial contraction.

In the first case mentioned by Dr. Sachs, he showed that the solid solution, single crystal, elongates by slip along the {111} planes, which are more favorably disposed to the maximum resolved shear stresses, and that the round cross section of the bar changes to an elliptical cross section. That was also true of the material that had reached only the first aging peak, but was not, however, true of the material that had reached the final peak.

It would seem that since the initial peak is due to plastic deformation and consequent precipitation only along slip bands, and since no general precipitation has taken place as yet, there is not enough interference to prevent slip clear across the sample on a {111} plane. In other words, the change in shape should correspond roughly to that obtained when pulling a solid solution sample. When, however, general precipitation has occurred throughout the whole grain, slip apparently is interfered with to a greater extent, and does not traverse the whole cross section of the sample on a single {111} plane.

Dr. Sachs also mentioned the ordered arrangement or superstructure; that is, the migration of the solute atoms into specific places in the solvent lattice. Dr. Gayler also mentioned that in her recent paper. If such a migration of the solute (copper) atoms is assumed, into definite locations in the solvent (aluminum) lattice such as occurs in the copper-gold, then should not there be expected a different change in electrical conductivity than is actually obtained? That is, the conductivity of a disordered material is lower than that of the ordered material. In other words, if there is a tendency toward the formation of an ordered arrangement of the solute atoms during the early states an increase in conductivity would be expected. This is contrary to experimental results.

Mr. Wise brought out some examples of aging curves having inflection points that change as gold is replaced by palladium, or vice versa, in a gold-palladium-silver-copper alloy. It is quite possible, of course, in such a complex alloy that more than one phase might precipitate, thus producing two peaks in the aging curves.

Dr. A. J. Smith brought up the question of degree of plastic deformation produced during quenching. We have no actual measure of the amount of plastic deformation, but we do know that a large as-quenched grain is far from being a perfect single crystal. That is, you can mount it, take an X-ray reflection pattern and show that the spots are diffuse as a result of plastic deformation during the quenching. But when you repeatedly reheat, and quench between heatings, there is apparently no change in orientation. That is, the amount of deformation that was produced was insufficient, apparently, to cause any rotation of grain fragments that may lead to recrystallized grains of a new orientation.

Dr. Harrington mentioned resistivity measurements. The same alloys on which we have reported here are being investigated using time-resistivity curves to follow the course of the aging. We are also using dilation measurements to follow the course of aging, and it is hoped that in the near future we will be able to correlate all of these various methods of analysis.

L. W. KEMPF,* Cleveland, Ohio.—The author's explanation of the double hardness peaks is most satisfactory. The authors again indicate their preference for the precipitation-hardening theory originally proposed by Merica, Waltenberg and Scott. It might be advantageous to consider the new data developed by Fink and Smith in connection with the original precipitation-hardening theory.

Finding microscopic evidence of a precipitated phase considerably prior to the attainment of maximum mechanical properties and prior to appreciable changes in lattice parameter, Dr. Fink and Dr. Smith previously concluded that there was "no justification for modification or complication of the theory of precipitation hardening advanced by Merica, Waltenberg and Scott." The authors have not given their interpretation of this theory. It is to be assumed, therefore, that they conclude with Merica, Waltenberg and Scott[1] that hardening in aluminum-copper alloys " . . . during aging is actually accompanied by a phase change within the alloy. In so far as it can be said then that this phase change causes the hardening, for the reason that it accompanies it, this phase change may be regarded as its active cause."[10] Taking as an approximate definition of a phase: " . . . a portion of an alloy physically and chemically homogeneous throughout which is separated from the rest of the alloy by distinct bounding surfaces,"[11] it is believed some investigators would disagree with the limitation imposed by a strict adherence to the original precipitation-hardening theory. The authors' own data seem to be capable of being interpreted at variance with this theory.

It would appear that in the hardening of aluminum-copper alloys rapidly cooled from elevated temperatures, we are dealing with at least two different aging rates, one of which, applying to relatively severely deformed metal, might be represented by curve *A* in Fig. 2. Another aging rate characteristic of metal deformed considerably less might be illustrated by curve *B* in the same figure. From the data in the present paper, there can be no doubt but that precipitation occurs at greatly differing rates in various portions of the same crystallite. In these instances the differences in rates of precipitation were undoubtedly largely concerned with variations in the amount of plastic deformation. Apparently precipitation in the deformed material of the slip bands proceeds at such a great rate that softening, as indicated by the valleys in the curves of hardness versus time, occurs before hardening takes place generally throughout the matrix. Is it not conceivable, therefore, that the precipitate that is visible prior to the attainment of maximum properties is formed under the conditions somewhat as represented by the latter portions of the curve *A* in Fig. 2 while the maximum mechanical properties may be the result of a much slower rate of precipitation, unaccompanied by visible particles, applying to the major volume of the alloy? It may be significant as indicated in the curves of Fig. 2 that the final maximum hardness of curve *C* is contributed to but slightly by the hardening illustrated by curve *A*. It is also not inconceivable that other factors markedly affect precipitation rate; for example, precipitation generally proceeds much faster in the grain boundaries than within the grain. The presence of crystal imperfections or insoluble particles may also conceivably so affect precipitation rates in their immediate neighborhood as to bring about the precipitation and growth of particles to microscopic size without greatly affecting the macroscopic hardness.

The authors say (p. 228): "Since, as previously pointed out, slow quenches produce less plastic deformation in the alloy samples, it is more difficult to detect evidences of initial precipitation in these samples because of the lack of a readily detectable pattern. In the samples quenched in oil at 100° C. and aged at the same temperature, precipitation could not be definitely revealed even after 384 hr." Under these conditions it should be noted, however, from Fig. 15, that considerable hardening has taken place and that the tensile strength has even begun to show the decrease characteristic of overaging. Similarly, the first microscopic evidences of precipitate in specimens quenched in oil at 153° C. are observed only after 8 hr. at this temperature, at which time the major portion of hardening has occurred. It is perhaps also significant in connection with the water-quenched sample of the 4 per cent copper alloy that, although particles of visible precipitate could be noted after 5 min. at 100° C., continued aging up to 384 hr. did not appreciably change the microstructure, although most of the hardening took place between 1 and 300 hr. It would appear that the particles that were observed after 5 min. at 100° C. were the result of precipitation under unusually favorable conditions; for example, along plastically deformed slip bands, while the major portion of the hardening was unaccompanied by visible precipitation. The authors show, in Figs. 11 and 12, that the water-quenched 5.17 per cent Cu alloy shows precipitation within a relatively short time at room temperature and even that the amount of this precipitate may increase with time up to 31 hr. They could, however, observe no change in microstructure between 31 hr. and 3 months, although it is known that hardening in this alloy continues throughout this period.

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* Aluminum Company of America, Aluminum Research Laboratories.

[10] Nat. Bur. Stds. *Sci. Paper* No. 347 (1919).

[11] National Metals Handbook (1936) 252. Amer. Soc. Metals.

In conclusion, it is believed that the new data presented here, together with other well established observations such as, for example, the softening on heating at elevated temperatures following room-temperature aging, the generally better corrosion resistance of alloys (particularly of aluminum) aged at room temperature compared with those aged at elevated temperatures, and the changes in electrical resistance accompanying hardening in many precipitation-hardening alloys, cannot be adequately explained on the basis of the so-called simple precipitation-hardening theory involving the keying of slip planes primarily by particles of a phase, the thermodynamic state of which is definable, precipitated from the supersaturated solid solution. Definitions of "precipitation" and "precipitate" broad enough to include any alteration of the supersaturated solid solution or any concentration of solute atoms, respectively, would embrace all the available data. This conception, however, can hardly be deduced from the original description of Merica, Waltenberg and Scott's theory, particularly since their theory was originally based on the relationships implied in phase or state diagrams, and the phenomena here being considered cannot yet be defined in this manner. A more definite statement from the authors regarding their views would prevent confusion.

G. Wassermann,* Frankfurt a.M., Germany (written discussion†).—Fink and Smith's study is certainly one of the most important and interesting upon the hardening of aluminum alloys that have appeared in recent years. In some experimental investigations upon the hardening of aluminum-copper alloys which I recently carried out,[12] the appearance of precipitation in the form of rectilinear bands, such as Fink and Smith had already noticed, was confirmed. However, some differences from their determinations were shown with respect to the time of the first appearance of the precipitation. While they found distinct precipitation in the new investigation at 150° C. after only 2 min., it was not possible for me to ascertain any precipitation during the first hours of the hardening. The polished specimen rather remained entirely clear, and the first precipitation became visible only after 15 to 20 hr., and thus at the same time when the beginning of the precipitation was also indicated radiographically through change of the lattice constant.

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* Metallgesellschaft.

† Translated from the German.

[12] *Ztsch. Metallkunde* (1938) **30,** No. 2.

Concerning the authors' mechanical tests, it is not clear to me how a maximum of mechanical qualities can be determined after so short a drawing period as some minutes, as variations of the individual results occur constantly in mechanical testing and, with drawing periods of a few minutes, the duration of the heating has still considerable influence.

With respect to the interpretation of the tests, the determination that the quenching stresses have an effect upon the precipitation appears to be very important. However, the explanation that the bands that appear in the crystals are slip bands is therefore not very satisfactory, because such wide slip bands would suppose a great plastic deformation, which would scarcely be possible as a result of the quenching. In opposition to this, reference may be made to an interpretation of the banding, which was originated by Professor E. Schmid, and which says that the bands result from mechanical twinning during quenching. Actually, it appears that mechanical twins are visible in large numbers on a polished surface after quenching from 525° C. These twins are then the same in which the precipitation occurs.

Concerning the causes of the hardening, it may be said that no reason appears to me, from my own investigations, for abandoning the assumption that hardening at low aging temperatures is not caused by precipitations.

While Fink and Smith's results and views can therefore not be confirmed at all points, it is undoubtedly a great service that they have again made the microscope a valuable aid in the investigation of the hardening of aluminum alloys. After the first negative results, it was believed for years that nothing was to be seen in the microscope during hardening. Today it is seen that this idea was incorrect.

M. L. V. GAYLER,* Teddington, England (written discussion).—The authors have put forward an explanation of the double peaks in hardness curves based on the fact that plastic deformation occurs locally at grain boundaries and along slip planes, and have demonstrated this fact by their excellent photomicrographs. They consider that "the first peak in the aging curves of these alloys can be explained simply by the more rapid precipitation in the regions that have experienced plastic deformation by quenching. The softening that follows the first hardening may be due to overaging in these regions." In contradistinction to the views put forward by Cohen and myself in our recent papers, which first demonstrated that a relation existed between the two different kinds of aging taking place during age-hardening, the present authors consider that the simple precipitation theory accounts for the facts described.

However, the formation of an intermediate phase during age-hardening—or, rather, the rearrangement of the atoms within the lattice to form, ultimately, such a phase prior to the precipitated phase proper—does not appear to be a simple precipitation process. The precipitation demonstrated in the photomicrographs submitted by the authors has yet to be shown to be $CuAl_2$ before the authors' explanation is proved.

It is surprising, however, that no reference has been made to the very valuable research by Phillips and Brick[13] on quenching strains on similar high-purity copper aluminium alloys, since, by a different method, they demonstrated very clearly that "the rate and magnitude of the age-hardening process is greatly influenced by the quenching speed." They made also the important statement: "It seems likely that the age-hardening at room temperature is related in an unknown manner to a partial relief of the original quenching strain. Although the parameter of the quenched specimen has decreased slightly, it is still considerably above that of the non-aging, air-cooled specimen, and it seems possible that the relief of strain has been accompanied by an actual precipitation. With one exception, the lower the lattice-parameter value of the quenched alloy, the less the magnitude of room-temperature age-hardening. Although our data suggest the possibility of an actual precipitation, the evidence is admittedly too meager definitely to establish this point." Fink and Smith, by their photomicrographic work, have shown that the deductions of Phillips and Brick are correct. The correlation between these two investigations should not have been missed.

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* National Physical Laboratory.

[13] A. Phillips and R. M. Brick: *Trans.* A.I.M.E. (1934) **111,** 94.

The authors' evidence in support of two peaks existing during room-temperature aging is, however, not entirely convincing. In Fig. 13, the curves through points representing the mechanical properties have been drawn in a rather arbitrary manner; the mean of differences of adjacent readings—well outside experimental error—have been given in one case but not in another. The authors' results may be interpreted as in Fig. 22, which takes recognition of the fact that marked differences in adjacent readings are probably due to inhomogeneity of the material itself. For these reasons I do not feel the authors are justified in deducing that two maxima occur during room-temperature aging. If one maximum is considered to occur after 200 hr., surely a second maximum is indicated after 1000 hr., which, however, the authors ignore.

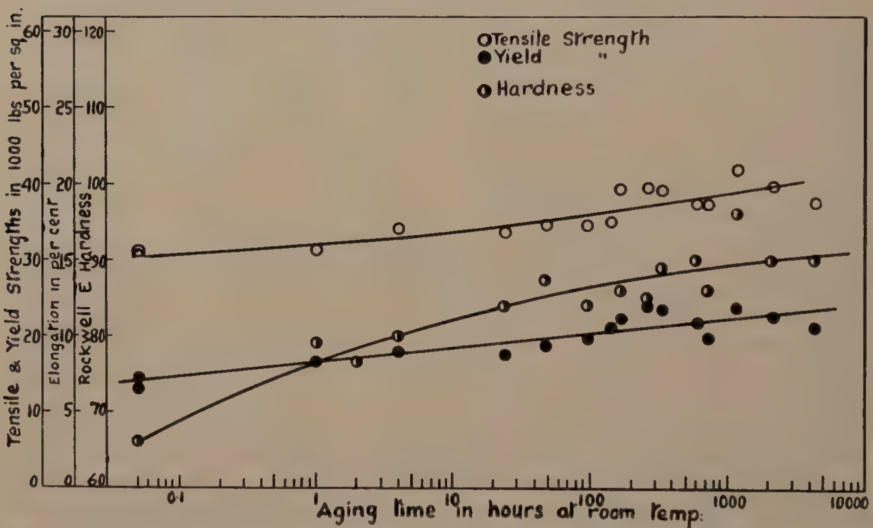

FIG. 22.—PLOT OF AGE-HARDENING DATA OF AL-CU ALLOY (4 PER CENT CU) QUENCHED IN WATER AT 25° C.

W. L. FINK AND D. W. SMITH (written discussion).—The discussions both written and oral, particularly Mr. Kempf's, indicate that we have not presented our conception of the mechanism of age-hardening with sufficient clarity. A brief description of our conception of changes taking place during age-hardening will therefore facilitate answering the questions raised in the discussion.

We will restrict our consideration to the age-hardening of high-purity binary aluminum-copper alloys. When such alloys are held for a sufficient length of time at a temperature above the solid solubility limit, the copper goes into solid solution; i.e., the copper atoms are distributed at random on the aluminum lattice. As a result of thermal agitation, the copper atoms are, of course, moving from point to point on the lattice. In any given region, therefore, the concentration of copper atoms is constantly changing. At any given time there will be regions where the concentration of copper atoms will be high. However, such groupings are not stable at this high temperature, and they immediately disintegrate. Upon quenching, the structure that existed at the solution heat-treating temperature is retained. At the aging temperature, however, groupings of copper atoms having a configuration similar to that in the θ or θ' phase (depending upon aging temperature) will be stable. The minute stable particles thus produced would be described by the colloidal chemist as "a disperse phase." It is undoubtedly in this sense that Merica, Waltenberg and Scott used the term "phase change," since in another part of their article they say, " . . . precipitation of the $CuAl_2$ takes place in the form of very fine particles of colloidal dispersion."

This conception of the formation of the disperse phase is substantially the same as that presented by Einstein, a translation of which is given in the first volume of Alexander's book on colloid chemistry.[14] However, Einstein's treatment applies generally to both liquid and solid particles. In the particular case under consideration—the age-hardening of aluminum-copper alloys—the disperse phase is a crystallogen and we can give a more detailed description of the mechanism of its formation. The well-known work by Mehl and his collaborators has elucidated the Widmanstätten mechanism by which crystalline precipitate particles are formed from a crystalline solution.

Obviously, the probability of the formation of small particles by the chance association of copper atoms is much greater than the probability of formation of larger particles under any given set of conditions. Consequently, we would expect most of the precipitate particles to be initially the smallest size that is stable at the aging temperature in question. It would be expected that the lower the aging temperature, the smaller the initial stable particles.

Once a stable particle of θ or θ' is formed, it can grow by the normal and simple process of diffusion of copper atoms in the solid solution to the interface. As the copper atoms at the interface attach themselves to the precipitate particle, the concentration of copper atoms in the adjacent solid solution is diminished. Therefore, diffusion of copper atoms into this region is the normal type of "downhill" diffusion.

In the early stages of the aging process, the precipitation is highly localized, and the individual particles are small in size and number. Consequently, the effect on the physical properties is slight. It is probable that many of the particles could experience considerable growth and increase in number before any change could be measured in tensile properties. In the aluminum-magnesium alloys, some particles, particularly at the grain boundaries, grew to such a size that they could be resolved clearly under the microscope before any change in yield strength or lattice parameter could be measured. When a sufficient number of these precipitate particles have grown to a sufficient size, the physical properties are altered considerably.

According to the modern theory of the metallic state, maximum electrical resistivity would be expected when the maximum number of particles have attained a size comparable to the wave length associated with the electron. Consequently, one of the first changes to be observed as the particles grow would be an increase in the electrical resistivity provided the initial particle size is less than the wave length of the electrons. Obviously, as the particles increase still further in size, the electrical resistivity decreases.

The density changes that occur during the aging process are functions of two factors—the densities of the phases involved, and the disregistry of the lattices at the interfaces, which gives an effective lower density in this region. It would be expected that particles of θ' so small that registry between the lattice of these particles and the aluminum solid solution is good would result in negligible changes in density of the alloy as a whole. As the particles increase in size, the density of an aluminum-copper alloy should decrease on account of greater disregistry at the interface, and because a concentrated solution of copper in aluminum has a smaller volume than the θ' phase and dilute solution into which it decomposes. The decrease in density that occurs in alloys of aluminum and copper containing silicon and other impurities should not be confused with the aging of high-purity binary aluminum-copper alloys.

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[14] J. Alexander: Colloid Chemistry. Chemical Catalogue Co., 1926.

As the particles of precipitate grow, there is more and more interference with slip or plastic deformation. In other words, the hardness, tensile strength, and yield strength increase. Apparently, some of the discussers have gained the impression that we believe hardening is caused only by particles that are visible microscopically. We have never intended to give such an impression. We agree with Merica, Waltenberg and Scott, and Jeffries and Archer that the critical dispersion that produces maximum hardening is a colloidal dispersion.

We have used the presence of visible precipitate in two ways:

1. To disprove the opinion previously held by many that absence of change in lattice parameter could be used as proof of the absence of precipitation, the most potent argument in favor of a pre-precipitation theory.

2. Before particles are large enough to be seen microscopically, there must be particles of smaller size. In other words, pre-precipitation phenomena, if they existed, would be relegated to a stage in the aging process so early that no measurable change in hardness, tensile strength or yield strength could be attributed to them.

Sachs admits that the X-ray tool is not sufficiently sensitive to prove the existence or absence of a small amount of a second phase. He contends, however, that the amount of precipitation is insufficient to explain the changes in physical properties. We consider that there are at least two fallacies in Sachs' argument. In the first place, we believe that he has greatly underestimated the possible amount of precipitation, and in the second place, emphasis should be on the number of particles of precipitate within a certain range of sizes rather than upon the total amount of the phase precipitated.

Sachs' estimate of the maximum amount of copper that could precipitate without detection is another way of saying that it would be possible to obtain visible diffraction lines in a back-reflection pattern from approximately 1 per cent of the solid solution lattice which had suffered different amounts of decomposition. This would not be possible even if the decomposed regions were rather large in size and were free from strain. It is probable that conditions that actually obtain during aging would require at least 10 times as much precipitation as Sachs' maximum estimate.

In regard to the second point, binary aluminum-nickel alloys containing 0.03 per cent of nickel and binary aluminum-beryllium alloys containing 0.07 per cent of beryllium, show approximately the same relative increase in hardness upon aging as the binary aluminum-copper alloys containing 4 to 5 per cent copper. These examples are cited to show that the quantity of precipitate is not the criterion of the extent of age-hardening. The principal factor is the number of particles of precipitate within a certain range of sizes.

Mr. Kempf expresses the opinion that the softening on heating at elevated temperatures following room-temperature aging, and the generally better corrosion resistance of aluminum-copper alloys aged at room temperature compared with those aged at elevated temperatures cannot be adequately explained on the basis of the simple precipitation theory. Actually, G. Masing[15] has given a very good explanation of softening during artificial aging subsequent to room-temperature aging. His explanation is that the smallest particles that are stable at room temperature are not stable at the higher temperatures. Consequently, the first effect of raising the aging temperature is to destroy these smaller particles. This would, of course, result in softening.

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[15] G. Masing: *Trans.* A.I.M.E. (1933) **104,** 13.

In regard to the type of corrosion depending upon the aging treatment, it is our belief that the precipitation theory agrees with the experimental facts. Intergranular corrosion is caused principally by electrolytic solution of a continuous layer of solid solution at the grain boundaries which has suffered enough preferential decomposition to produce a substantial difference between its solution potential and that of the bulk of the sample. When a sample is aged at such a low temperature or for such a short time that the regions depleted in copper are much smaller than the distance between precipitate particles, no such continuous layer would be formed, and intergranular corrosion would not occur. Further growth of the θ' particles would cause growth of the depleted regions till they finally overlap. Since precipitation is most rapid at the grain boundaries, a continuous layer of solution depleted in copper would first form there, and intergranular corrosion would occur. Further aging would result eventually in a uniformly depleted solution throughout the sample, eliminating the difference in solution potentials, and no intergranular corrosion occurs. Corrosion tests on the specimens used in this investigation exhibit the above changes.

Gayler's conception of the intermediate phase that has been designated θ' evidently does not conform with that of Wassermann and Weerts' or with the authors'. θ' is a distinct phase, which has a characteristic X-ray diffraction pattern. Our explanation of the age-hardening process has been based consistently on the precipitation of the θ' phase at the low aging temperatures.

This short paper was devoted to an explanation of double aging peaks in terms of the precipitation theory of age-hardening. No attempt was made to review literature pertaining to the age-hardening problem in general. For this reason, the paper of Phillips and Brick, as well as many other pertinent papers, was not mentioned.

Gayler has criticized the manner in which the curves of Fig. 13 were plotted. Consequently, a few details showing why the curves were drawn in this manner will be given. The points up to 1000 hr. represent two different experiments. The values of tensile strength, yield strength, and elongation in both experiments showed the presence of maxima (or minima) at about 200 hr. Consequently, the curves were drawn to show this feature. Hardness measurements on coarse-grained materials show considerable scatter, so that no maximum could be definitely identified in the hardness curve. The points beyond 1000 hr. are the result of a single experiment. It is true that there is a suggestion of maxima at about 1000 hr. However, we consider the data too meager to draw a definite conclusion that such maxima exist. For this reason, they were not shown on the curves.

It is not particularly surprising that Wassermann was unable to reveal precipitation at as early a stage as was indicated in our paper. The technique developed in the Aluminum Research Laboratories is the result of years of work. However, several workers, both on and outside of the Laboratory staff, have learned how to reveal precipitation in these alloys after the times indicated in our paper. Success depends upon preparing a polished surface with the minimum of surface flow, as well as the use of a suitable etching technique. The practice followed in determining physical properties after short aging periods was as follows: After the specimen had been in the oil bath for the time indicated, the specimen was quickly removed from the bath and placed in water at room temperature. As soon as the specimen had attained room temperature, it was removed and tested.

Wassermann is of the opinion that plastically deformed portions of the specimen are twins rather than slip bands. We considered this possibility but rejected the idea because no twins could be detected microscopically after the specimen was repolished. Moreover, twins would represent new orientations, which should give rise to polycrystalline material on reheat treatment. This was not observed either in our work or the work reported by Mr. A. J. Smith in the discussion of this paper.

Cohen points out that water-quenching should decrease the maximum hardness and strength attainable by aging because it promotes nonuniformity of precipitation and thereby fewer particles simultaneously reach critical size for maximum hardening. It may be that such a relation actually exists, but that the difference is too small to determine experimentally. There is also the possibility that this factor tending to decrease the hardness of water-quenched material is counterbalanced by the more rapid formation of nuclei in the unstressed regions of the water-quenched sample than in the oil-quenched sample. The number of visible particles per unit area in samples that have been aged long enough to produce microscopic particles indicate that this may be true.

The Gold-aluminum System

By Arthur S. Coffinberry,* Student Associate, and Ralph Hultgren,† Junior Member, A.I.M.E.

(New York Meeting, February, 1938)

We have studied the gold-aluminum system by X-ray diffraction and by the microscope over the entire range of composition for temperatures between 300° and 500° C. Results obtained are shown in Fig. 1, combined with the work of Heycock and Neville[1] at higher temperatures. The diagram differs in important details from that given by Hansen[2] in his critical compilation of the literature of binary alloy systems.

This work was undertaken both because of the intrinsic value of a knowledge of the phase diagram of this system and because of the need of theoretical metallurgy for precise and accurate data, particularly X-ray diffraction data.

Systematic studies of equilibrium diagrams, particularly by Hume-Rothery,[3] have shown regularities that yield a certain insight into the nature of alloying forces. It has been shown, for example, that solid solubility depends on the concentration of free electrons in the alloy, on the relative radii of solvent and solute atoms, on the forces of attraction between atoms, and on the relative stability of intermediate phases. The well-known Hume-Rothery rule states that the crystal structures and compositions of many intermediate phases depend on the electron-to-atom ratio. This has been confirmed and extended by wave mechanical calculations.[4]

A knowledge of the forces between atoms in alloys, even an imperfectly developed empirical one, should be a valuable guide in the preparation of technological alloys of desirable properties. Furthermore, such information is basic in such problems as rate of diffusion, age-hardening, phase transformations, and others. The most valuable data for this purpose are furnished by X-ray diffraction studies. Unfortunately, work has been

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Most of the material presented in this paper was abstracted from a thesis submitted by Arthur S. Coffinberry in partial fulfillment of the requirements for the degree of Doctor of Science, Harvard University, 1937. Manuscript received at the office of the Institute Dec. 1, 1937.

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[1] References are at the end of the paper.

carried out extensively only on gold, silver and copper binary alloys with low-melting metals, and even on these not completely. Considerable progress in the theory of alloying must wait on the accumulation of data.

One of the important systems that has never been completely studied by any method is the gold-aluminum system. It was first studied by Roberts-Austen[5] about 1890. At that time he was already attempting to correlate alloy properties with atomic volumes. He described the purple compound $AuAl_2$, noted its high melting point and the fact that it formed with a large evolution of heat.

In 1900, Heycock and Neville[1] determined the liquidus curve completely. This was one of the first investigations in which the microscope was used along with thermal analysis. These workers applied X-rays to a study of alloy systems for perhaps the first time when they obtained excellent radiographs of samples that contained $AuAl_2$ in a soft aluminum matrix, and which were difficult to polish. Their liquidus curve indicated the existence of five intermediate phases, which we shall hereafter refer to as beta, gamma prime, delta, zeta and eta. They considered these phases to have the compositions Au_4Al, Au_5Al_2 or perhaps Au_8Al_3, Au_2Al, probably $AuAl$, and $AuAl_2$, respectively.

In 1914, Heycock and Neville began work on the solid part of the system but failed to complete it. They determined the solidus line of the alpha phase and a solid solubility of aluminum in gold, although they were not satisfied with the latter. They also determined the phase boundary of the beta phase and found that it decomposes below 420° C. into alpha plus gamma, which react below 400° C. to form beta prime. They concluded that beta prime was really stable up to 520° C. because it would not decompose on heating until that temperature was reached, and because its formation from the beta could be artificially induced at 515° C. and below.

Apparently no more work has been done on this system except for the determination of the crystal structures of two intermediate phases. Westgren and Phragmén[6] found the beta prime phase to be isomorphous with beta manganese. They assigned to it the formula Au_3Al to agree with the Hume-Rothery rule, instead of Au_4Al given by Heycock and Neville. West and Peterson[7] studied the purple eta phase $AuAl_2$, and found it to have the calcium fluoride structure.

Dehlinger[8] and others[3,9] have listed the compound Au_5Al_3 with a close-packed hexagonal structure in agreement with the Hume-Rothery rule. We found that no such compound exists. The reference cited by Dehlinger does not mention gold-aluminum.

METHODS AND MATERIALS

The gold used was purchased in part from the General Plate Co., of Worcester, and in part from the American Platinum Works, both pieces said to be 99.975 per cent pure. The lattice constant was $a_0 = 4.0702$ Å., agreeing well with Jette and Foote's[10] value, $a_0 = 4.0704$ Å. for pure gold.

The aluminum was kindly furnished by the Aluminum Company of America, which reported that it contained 0.005 per cent Si, 0.003 per cent Fe, and 0.004 per cent Cu. Its lattice constant, $a_0 = 4.0415$ Å., also agreed well with Jette and Foote's value, $a_0 = 4.0414$ Å.

Attempts to prepare the alloys in sealed-off evacuated Vitreosil tubes failed because of excessive reaction of aluminum with silica, producing alumina and metallic silicon. Therefore small crucibles of pure aluminum oxide, 1 cm. in diameter and 2 cm. tall, were accordingly purchased from the Lava Crucible Co. of Pittsburgh, which made them to our order. The crucibles were said to be: "98 per cent Al_2O_3, the largest impurity being TiO_2 with a very small amount of Fe_2O_3 and SiO_2." The crucibles proved to be very satisfactory. Melts made in them showed no trace of silicon under the microscope. Metallic aluminum melted in them showed no change of lattice constant.

It was found to be difficult to melt high-aluminum alloys in a vacuum furnace because the aluminum particles frequently refused to coalesce, owing to a protective film of oxide. After some trial, the following technique was adopted.

An aluminum oxide crucible containing a weighed amount of gold was lowered into a platinum-wound resistance furnace at a temperature of about 1200° C. After the gold had melted, a single piece of aluminum of the correct weight was dropped into the crucible. The heat of the reaction immediately raised the melt to a white heat and the crucible was withdrawn from the furnace at once. Usually a thorough mixing of the metals occurred. If any gold appeared to be segregated at the bottom of the ingot, the extra precaution was adopted of inverting and remelting it, so that the heavier gold had to sink through the aluminum. The microscopic and X-ray examination described below showed that in every case equilibrium was attained by the homogenizing anneal except for the peritectic reaction noted.

This homogenizing anneal was carried out by sealing a number of ingots, each weighing from one to two grams, in an evacuated Pyrex tube, placing the tube in a furnace and holding the furnace at a temperature of 20° to 50° below the solidus for two to six weeks. The ingots were separated from one another by small quantities of washed and ignited asbestos. Ductile ingots were cold-worked before annealing. Shorter anneals would perhaps have been adequate to obtain homogeneity, but it proved convenient to anneal for long periods.

Chemical analysis of representative samples for both gold and aluminum checked so closely with the quantities weighed out that it was thought unnecessary to analyze all samples. Any appreciable variation in composition of one of the samples would have been detected by yielding results inconsistent with the others.

A section of most of the ingots was polished, etched, and examined microscopically. All results were concordant with X-ray photographs. This work was particularly useful in the range between 44 and 50 atomic per cent aluminum, where three phases are present because of an incomplete peritectic reaction.

Heycock and Neville[1] had found three phases in this region up to 66 atomic per cent aluminum. In general, we fully corroborated all of their observations.

We tried bromine water as an etchant in addition to a mixture of sodium cyanide plus ammonium persulphate. The bromine water was the better, and gave satisfactory results everywhere except in systems containing $AuAl_2$. Fortunately, the brilliant purple color and hardness of this constituent made etching unnecessary.

X-RAY WORK

The homogenized samples were filed, or pulverized in a diamond mortar, depending on whether they were ductile or brittle. They were then sealed off in evacuated Pyrex tubes and given a final anneal at carefully controlled temperatures for periods varying from 24 hr. to a week, depending on the temperature of anneal. The glass tubes were suspended on an asbestos string in a vertical resistance furnace controlled within perhaps 3° C. by Brown pyrometers through chromel-alumel thermocouples. Accuracy of instrument and thermocouple was checked against the melting point of pure zinc. Anneals were made at temperatures varying between 300° and 500° C. The composition and temperature of each anneal is indicated by crosses in Fig. 1.

In order to secure uniform temperatures and a low temperature gradient within the furnace, the following arrangement was used. Inside a vertical 1½-in. Vitreosil tube furnace were placed four nichrome tubes 5⁄16 in. inside diameter and 2 ft. long. The middle 4 in. of these tubes was surrounded by a considerable mass of copper, a solid cylinder in which holes were drilled to accommodate the tubes. The control thermocouple was also inserted in a hole in the block, but actual temperatures inside the nichrome tubes were checked by a standardized thermocouple. The copper block was nickel-plated to aid in protection against oxidation. The temperature gradient was found to be 2° C. for the middle 3 in.; less than one degree for the middle inch.

Upon completion of the anneal, the glass tubes containing the samples were expelled and broken under water on an anvil by suddenly ramming a steel rod through the nichrome tube. A very rapid quench was thus obtained.

Debye photographs of samples covering the whole range of composition confirmed the fact that there were five intermediate phases. In order to determine phase boundaries more exactly, X-ray diffraction photographs were taken in a symmetrical back-reflection focusing camera. Back-reflection lines are particularly sensitive to small changes in lattice parameter, hence to changes in the composition of the phase giving rise to the lines. Wherever the crystal structure of the phase was known, the lattice parameter was calculated by the method of Cohen.[11] Where the crystal structure was not known, films were compared directly to see if any shift of line positions had taken place. By these means, we have

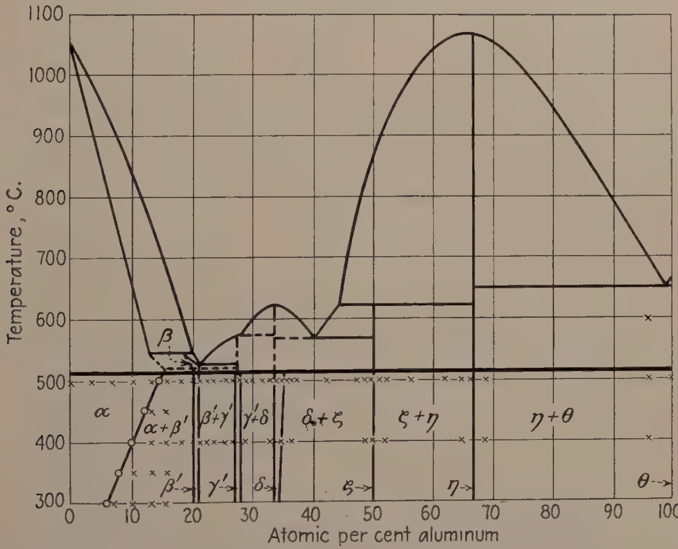

Fig. 1.—The gold-aluminum phase diagram.

Crosses indicate samples tested in the present work. The diagram above 500° C. is taken from Heycock and Neville's work.

determined phase boundaries and compositions in most cases within a few tenths of a per cent.

Our results are shown in Fig. 1, combined with Heycock and Neville's liquidus and solidus curves. Their work on the beta phase and the beta-beta prime transformation is also shown. We have indicated that gamma prime is not formed by a peritectic reaction, a point on which Heycock and Neville were undecided.

Alpha Phase

Lattice constants were determined for various compositions and temperatures of annealing to a probable accuracy of better than one part in ten thousand. Results are shown in Fig. 2. Intersections of horizontal and slanting lines indicate solubilities at the various temperatures

(Table 1). They are considerably smaller than those given by Hansen.[2] He was probably guided by an admittedly uncertain value in Heycock and Neville's figures[1] and by analogy with the silver and copper-aluminum systems. Addition of aluminum to the alpha phase decreases the lattice constant almost five times as fast as predicted by Vegard's law, indicating a strong attraction between gold and aluminum atoms.

Table 1.—*Solid Solubility of Aluminum in Gold*

Temperature, Deg. C.	Solubility	
	Atomic Per Cent	Weight Per Cent
500	14.6	2.28
450	12.2	1.90
400	10.1	1.51
350	8.0	1.18
300	6.0	0.87

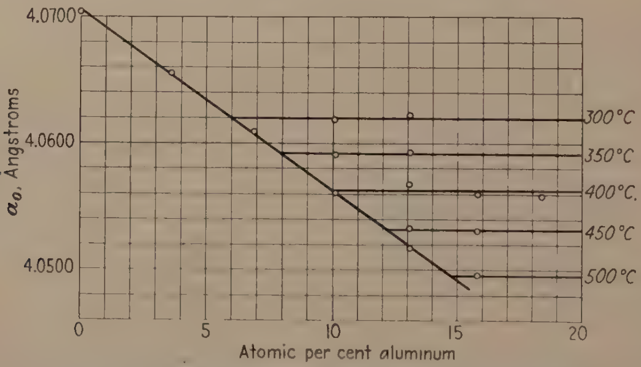

Fig. 2.—Lattice constant versus composition.
For various temperatures of anneal. The intersection of horizontal lines with the slanting one gives the solubilities at the various temperatures.

Beta-prime Phase

We confirm the results of Westgren and Phragmén[6] that this phase is isomorphous with beta manganese. The beta manganese structure is cubic with 20 atoms in the unit cell.

At 500° C. all samples containing 20 atomic per cent of aluminum or less were found to have the same lattice constant $a_0 = 6.9068$ Å., considerably closer than one part in 10,000, while the values with 21 atomic per cent aluminum and over clustered around $a_0 = 6.9049$ Å. This indicates a small range of homogeneity between 20 and 21 per cent. The decrease in lattice constant is about as much as that caused by the addition of 0.8 per cent Al in the alpha phase.

No trace of beta phase was found in any of the pictures, confirming Heycock and Neville's conclusion that beta prime is stable at these temperatures. A high-temperature X-ray camera is needed to investigate the beta phase.

Gamma-prime Phase

The crystal structure of the gamma-prime phase has not been determined. Its powder pattern resembles that of gamma brass in its general features and the structure is probably a distortion of the gamma brass cell. Similar distortions have been observed by Westgren[12] and co-workers but the nature of the distortion has not been worked out.

It is noteworthy that the line corresponding to (330) of the gamma phase is split into two very strong lines of equal intensity. This suggests that the cubic gamma cell is distorted into a hexagonal cell, since a tetragonal distortion should yield two lines of different intensities, while lower symmetries would give more than two lines. The symmetry seems not to belong to the rhombohedral division of the hexagonal system.

A small shift in position of back-reflection lines indicates a range of homogeneity between 26.7 and 27.7 atomic per cent aluminum. We estimate this extends from 27.0 to 27.7 per cent.

Heycock and Neville[1] had suggested from their liquidus curve that this phase might have the composition Au_5Al_2 (28.6 per cent Al) and be formed from a peritectic reaction. Their microscopic results, however, pointed to Au_8Al_3 (27.3 per cent Al), in better agreement with our results.

Delta Phase

The delta-phase structure is also unknown. Strong lines occur in the powder pattern in the same regions as the gamma-prime phase, but there are fewer lines. Shifting of back-reflection lines indicates a moderately large range of homogeneity extending from slightly less than 33.6 atomic per cent Al to about 35.0 atomic per cent at 500° C. At 400° C., the upper limit has fallen to about 34.6 atomic per cent, while the lower limit remains unchanged. The formula Au_2Al is approximately correct.

Zeta Phase

The powder pattern of the zeta phase is very complex and no attempt has been made to determine it. Since it is not hexagonal close-packed, we have avoided calling it the epsilon phase. The zeta phase is formed by a peritectic reaction that is difficult to carry to completion. Even after prolonged annealing three phases (delta, zeta, and eta) remain, in defiance of the phase rule, for compositions up to 49.9 atomic per cent Al. A 51 atomic per cent sample was diffuse and unclear, but for 52.1 per cent and over no trace of delta remained. There is no observable shift in back-reflection lines, hence probably no appreciable range of homogeneity. Its composition is quite possibly AuAl, as guessed by Heycock and Neville.

ETA PHASE

This brilliant purple phase has the crystal structure of calcium fluoride with $a_0 = 5.9868$. This structure was also found by West and Peterson,[7] who give $a_0 = 6.00$. The eta phase has an extraordinarily high melting point, even higher than metallic gold. It is quite brittle. There was no detectable change in lattice parameter for this phase in equilibrium with zeta as compared with it in equilibrium with metallic aluminum. Hence, there is no appreciable range of homogeneity. The composition is $AuAl_2$.

Hansen's[2] diagram shows a wide range of homogeneity for this phase (with question marks) guessed from slight evidence.

THETA PHASE

The lattice constant of this phase is practically identical with pure aluminum, from which it would be inferred that gold is practically insoluble in aluminum. The possibility should be recognized, even though unlikely, that the curve of lattice constant versus composition may be practically horizontal at this point, or in the zeta or eta phases, in which event the X-ray method would fail.

DISCUSSION OF RESULTS

An unusually strong attraction between gold and aluminum atoms is indicated by the large negative deviation from Vegard's law,[13] by the evolution of heat on mixing, and by the stability of intermediate phases, especially $AuAl_2$. This suggests that these forces are not purely metallic, but have a considerable ionic or covalent component. Brittleness and small range of homogeneity of intermediate phases bear this out.

The silver-aluminum system has a smaller negative deviation from Vegard's law and a simpler phase diagram. Thus, the forces between atoms seem to be smaller and more purely metallic. There are only two intermediate phases, both of them electron or Hume-Rothery compounds. One of them has the same structure as the beta prime of gold-aluminum but has the exact composition Ag_3Al with no range of homogeneity.

The copper-aluminum system, on the other hand, deviates farther from Vegard's law and has more intermediate phases.

The maximum solubility of aluminum in silver and copper is 20.4 atomic per cent in each case, considerably more than the 15 to 16 per cent we find in gold. Hume-Rothery and co-workers[14] have shown that the maximum electron concentration of alpha phases of gold, silver and copper with elements of the IIB, IIIB and IVB subgroups is about 1.4. Wave mechanical calculations[4] confirm this, indicating that the electron concentration should not be much greater than 1.36.

Our low value of 1.3 for the maximum electron concentration indicates the influence of other factors. A possibility is that the strong attraction of aluminum has increased the valence of some of the gold atoms above one. This is definitely indicated for the compound $AuAl_2$, as we shall mention later, and is also indicated by generally low electron concentrations throughout the system.

However, it should be remembered that phase boundaries are determined not by one but by two phases. Exceptional stability of the beta-prime phase would also reduce the solubility of aluminum in gold. The strong exothermic reaction noted by Heycock and Neville when beta prime is formed increases the plausibility of this idea.

The beta-prime phase is decidedly poorer in aluminum than the corresponding phase, Ag_3Al. Its electron concentration is only 1.41 electrons per atom, while 1.5 is called for by the Hume-Rothery rule. However, the wave mechanical calculation gives just 1.41 as the point where stability begins to decrease.

There is an interesting gradation in stability of beta-prime phases. In the copper-aluminum system there is no beta prime, in silver-aluminum it decomposes into alpha plus gamma at 390° C., far below the region of existence of the beta phase. In gold-aluminum, however, it is stable to 520° C., almost the melting point of the beta phase.

In the gamma-prime phase the electron concentration again just agrees with the wave mechanical value, 1.54, considerably below the empirical 21:13 ratio (1.625) for gamma phases.

The calcium fluoride structure of the eta phase, $AuAl_2$, resembles other compounds Mg_2Si, Mg_2Ge, etc., all with eight electrons to three atoms. This electron concentration is also derived from wave mechanics[4] for this structure. This suggests that gold may have a valence of two in this case instead of the usual value, one. Such an increased valence of gold would not be unreasonable in a field of highly attractive aluminum atoms, which may tend to pull one of the inner electrons of gold into the outer shell.

Dehlinger has suggested that this compound contains an Al_2 complex, which is electronegative to gold. This appears to be unjustified, since no such grouping occurs in the crystal structure and aluminum is ordinarily strongly electropositive to gold.

The very small solubility of gold in aluminum is probably due to the great stability of $AuAl_2$.

SUMMARY

The gold-aluminum equilibrium diagram has been determined at low temperatures. While it differs considerably from the diagram deduced by Hansen mainly from the experimental results of Heycock and Neville, it is not in conflict with those results.

A discussion of the diagram is given in the light of the theory of metallic structures. An unusually strong attraction between gold and aluminum atoms is indicated.

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DISCUSSION

(Frederic E. Carter presiding)

J. C. McDONALD.*—Was any microscopic temperature used to determine the solubility of gold and aluminum, or exclusively X-ray?

R. HULTGREN.—It was exclusively X-ray. We wished to work with powders, which were more rapidly quenched than solid samples.

F. E. CARTER,† Newark, N. J.—A most interesting thing in this alloy system is the $AuAl_2$ alloy, which is a very beautiful purple. Such a highly colored alloy is unusual. A patent has recently been taken out for use of this purple gold for jewelry purposes, by Degussa. Of course the alloy itself, $AuAl_2$, is completely unworkable, but by the addition of other metals it can be made somewhat workable. Strange to say, these additional metals include bismuth. It is rather extraordinary that bismuth added to aluminum-gold, a brittle alloy, will make the latter workable, but in addition to bismuth, silver, tin, zinc and cadmium can be added. This gives various color effects. The material is made by the powder metallurgy method.

Would it be possible to make a determination of the melting point of this $AuAl_2$? I know it is heresy to question Heycock and Neville's work, but it strikes me that, in determining melting points of alloys with so much aluminum, there is a possibility that their value is too high; that aluminum oxide may have formed to prevent the exact determination of the melting point. Their value has always seemed to me a bit too high.

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* Research Physicist, The Dow Chemical Co.

† Physical Metallurgist, Baker & Co., Inc.

E. M. Wise,* Bayonne, N. J.—It seems to me that the Degussa method is a means of bonding particles of nonductile $AuAl_2$ to produce a less brittle mass. $AuAl_2$ is extremely brittle and can be powdered with ease. I have attempted to get a modicum of ductility in alloys containing large amounts of $AuAl_2$ without success and also considered precipitating sufficient proportions of it from solid solution to yield a useful color—this also was unsuccessful. It is so stable and brittle the only hope is to stick it together with some low-melting material such as bismuth, perhaps. The compound does possess a beautiful color, and those who have not seen it ought to buy, beg, or borrow a bit of gold and make a small piece of it.

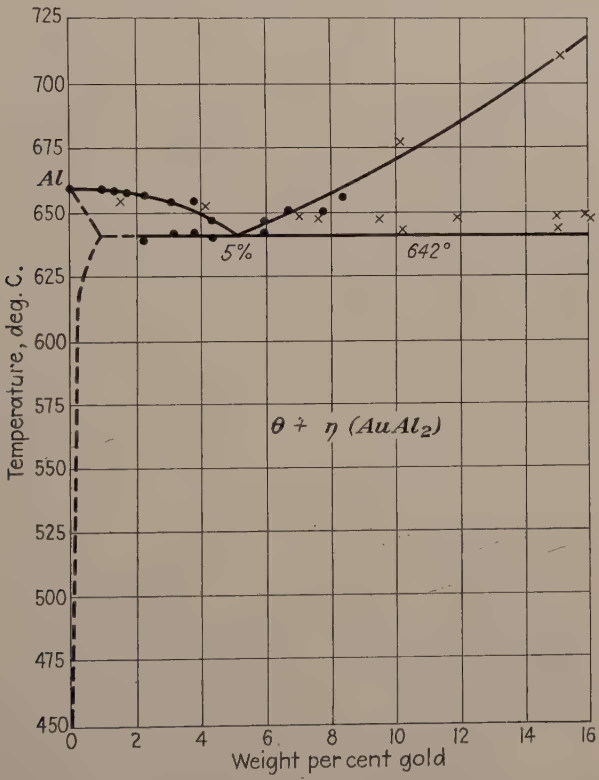

FIG. 3.—THERMAL ANALYSIS.
Dots indicate results by Ageew and Ageewa; crosses, those of Heycock and Neville.

F. E. Carter.—Generally in the gold-aluminum alloy, a fresh fracture is a different color from the surface of the alloy. According to the patent, apparently the aluminum must be very pure, and the alloy is always annealed in a vacuum or in nitrogen. The alloy really should be looked on as a nonmetallic material. It acts just as though it were glass.

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* Metallurgist, International Nickel Co.

R. Hultgren.—We have not any recent test on the height of the melting point. The bond is evidently very stable and forms with large evolution of heat; it might well have a high melting point.

N. Ageew* and V. Ageewa,* Leningrad, U. S. S. R. (written discussion).—Some years ago we studied the gold-aluminum alloys rich in aluminum. This research was not finished and the results were not published. We take this opportunity to communicate some of our experimental results and valuable data. Our investigation was made on the alloys in the range from aluminum up to 8.5 per cent Au, with a thermal method and by microscopical examination. The cooling curves were drawn on the Kurnakow registering pyrometer[16] with a 50-gram sample. The analyses of alloys were made by determination of gold. Microstructure could be examined without etching, as the purple compound $AuAl_2$ was well seen in the microscope. The results of the thermal analysis are given in Fig. 3, which shows that aluminum and the compound $AuAl_2$ form the eutectic at 5 per cent Au and 642° C. Our data are given as black points and those of the research of C. H. Heycock and F. H. Neville as crosses. Microscopical examination of these alloys showed that the solid solution can be formed only to 1 per cent Au, as all our alloys (from 1 to 8.5 per cent Au) contained the purple inclusion of the compound $AuAl_2$. The more exact determination of the solubility limit of gold in aluminum in solid state was not made.

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* Institute of General and Inorganic Chemistry, Academy of Sciences of U. S. S. R.

[16] *Ztsch. anorg. Chem.* (1904) **42,** 184.

Solid Solubility of Mercury in Silver and in Gold

By H. M. Day,* Junior Member, and C. H. Mathewson,† Member A.I.M.E.

(New York Meeting, February, 1938)

SILVER-MERCURY

The constitution of the system silver-mercury has attracted the attention of many investigators during the last two decades, but since their results are for the most part in poor agreement, there is little need for a review of their individual contributions. It remained for the very careful thermal and microscopic investigation of Murphy[1] in 1931 to give the constitutional diagram in its present and unquestioned form, which is shown in Fig. 1. He devised methods for taking cooling curves on alloys under high pressures and for the microscopic observation of alloys which contained liquid mercury as a structural constituent at ordinary temperatures. The compositions of the intermediate phases were confirmed and supplemented through X-ray analyses by Preston[2] and Stenbeck.[3] According to Murphy, at 276° C. silver is able to dissolve 44 to 45 weight per cent of mercury, which may increase at lower temperatures to about 50 per cent. Preston concluded that the saturation boundary occurred at 46 ± 2 per cent at 100° C. From the values reported in the literature, these are the only ones that may be accepted as lying even in the right region.

Preparation of Alloys

The silver used in the present investigation was supplied by the United States Metals Refining Co. through the courtesy of the Committee on Industrial Uses of Silver and, since a complete spectrographic and chemical analysis was furnished, no attempt was made to purify it or to further establish the impurities present. The analyses reported by the company are shown in Table 1. Milligan[4] has found that the magnesium content is probably less than 0.0005 per cent.

A part of a dissertation presented by H. M. Day to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Manuscript received at the office of the Institute Dec. 1, 1937.

* Metallurgist, Research Laboratory, General Electric Co., Schenectady, N. Y.

† Professor of Metallurgy, Yale University, New Haven, Conn.

[1] References are at the end of the paper.

Redistilled mercury which had been further purified by passing a stream of air through it was used in the preparation of the alloys. This method which effectively removes base metals by oxidation has been described by Alewijn.[5] In a note from the Bureau of Standards[6] it is reported that the presence of 0.001 per cent of metals such as zinc, tin, lead, cadmium, bismuth, copper, magnesium, or antimony so changes the mercury that it would by observation appear to be badly contaminated, but it was found that the presence of gold or silver even up to 0.1 per cent cannot be detected in this way. To supplement this evidence with regard to the purity of the mercury as well as to make certain that contaminations were not introduced in the process of making the alloys, a sample of the pure silver was compared spectrographically* with an amalgam containing 50 per cent Hg and with one of the same composition from which the mercury had been evaporated by careful heating. In neither instance were the lines of any impurity visibly strengthened over the corresponding lines in the pure silver. As a check on the possibility that gold or silver might be present in the mercury, a large amount

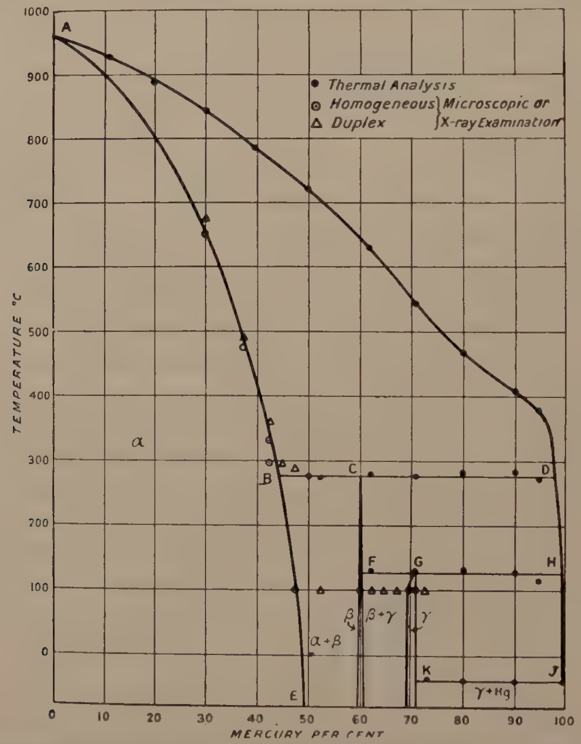

FIG. 1.—CONSTITUTIONAL DIAGRAM OF SILVER-MERCURY SYSTEM (MURPHY, 1931).

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* The authors are indebted to W. E. Milligan, Department of Metallurgy, Yale University, for all spectrographic analyses mentioned in this paper.

(25 grams) was weighed into each of two porcelain crucibles and slowly evaporated below the boiling point. After ignition below the melting point of silver the gain in weight was found in each case to be 0.002 gram. This indicated a gold and silver content totaling less than 0.001 per cent.

TABLE 1.—*Analyses of Test Material*

Element	Chemical Analysis, Per Cent	Spectrographic Analysis, Per Cent	Element	Chemical Analysis, Per Cent	Spectrographic Analysis, Per Cent
Au	0.001	0.001	Se	Nil	
Ag	99.993		Te	Nil	
Cu	0.0017	0.0020	Sn		0.001
Fe	0.0004	<0.0008	Ni		<0.0001
Pb	0.0003	0.001	Mn		Tr.
Bi	Nil	N.D.[a]	Mg		<0.005

[a] Not detectable.

Murphy has emphasized the "formidable experimental difficulties" he encountered when dealing with this system in which one of the components has a boiling point far below the melting point of the other. The natural consequence of this relationship is, of course, the volatilization of the low-boiling mercury in an unenclosed system, or the generation of extremely high pressures if the alloys are melted in a container with a limited volume. Since one of the most vital factors in the proposed investigation was the homogenization of the alloys, it was deemed necessary to produce them by solidification from the melt, as is the custom with metallic systems, even though rapid diffusion at lower temperatures might in time establish the same equilibrium.

It is perhaps needless to mention that the former method, in which the crystal types are intimately mixed throughout the ingot, is doubtless more amenable to a rapid change in the proportions of the two phases by annealing at different temperatures. Also, in view of the fact that many of the alloys are brittle and will not withstand a forming process, it seemed desirable to solidify them in shapes convenient for X-ray study. With these factors in mind, as well as the possibility of a more accurate synthesis than the subsequent analysis, the following technique was worked out.

Silver was rolled into the form of rod, which would just slip into fused silica tubing of 5-mm. bore. An amount of silver suitable to make an alloy ingot about 1¼ in. long was accurately weighed and inserted into a closed piece of tubing that had been thoroughly cleaned. In order to keep the unoccupied volume in the sealed tube as small as possible, and at the same time avoid loss of mercury when the seal was made close to the liquid metal, the tube was drawn down and constricted to a capillary just above the silver. The amount of mercury necessary to make an alloy of the desired composition was then introduced through the capillary by centrifugal action. The space around the silver was almost completely filled and, after evacuation to about 1½ microns, the tube could be quickly sealed off without warming the mercury. Provided that some care was exercised in the working of the fused silica, these metals could now be heated—to make certain that complete alloying had taken place—above the melting point of silver without an external pressure bomb such as described by Murphy.

To avoid the large segregation that would be incident to slow cooling in this system, the tubes were removed from the furnace above 960° C. and rapidly cooled in air. However, such a procedure yielded an ingot that had expanded on cooling to entirely fill the container, which obviously meant that the ingot was not sound, but full of gas pockets. This difficulty in producing a sound ingot was finally avoided by shaking the silica containers vigorously while the contents were freezing rapidly from the bottom. A theoretical discussion of these interesting freezing phenomena, which show a rise in pressure with rapid fall of temperature, is offered in our original paper.

For the determination of the lattice constant-concentration curve, alloys of the following compositions were prepared: 10, 20, 30, 35, 40, 45, 50, 52.5, and 55 per cent Hg.

With the exception of a preliminary 100-hr. anneal at 270° C., all the heat-treatments of the alloys are indicated in Tables 2 and 3. This preliminary anneal, as well as all those shown in Table 2, was carried out keeping the seal of the original silica tube unbroken, with the idea of insuring no change in the intended composition. X-ray examinations of the alloys 1A to 9A (10 to 55 per cent Hg) were made after 600 hr. at 270° C., but when the points calculated from these examinations appeared to be somewhat erratic and fell upon a curved rather than upon a straight line, the specimens were rolled and hammered until small surface cracks appeared. They were then sealed under vacuum in Pyrex tubes and returned to the anneal. The efficacy of deformation and the attendant recrystallization as an aid to homogenization is well known to metallurgists and is emphasized with special regard to silver alloys by Hume-Rothery.[7] Lattice parameters were measured after an additional 500 hr. at temperature, and, as a further check, specimens 3A and 6A (29 and 45 per cent Hg) were subjected to another hammering, machining, and 500° of anneal.

The anneals at 270° C. were controlled and periodically checked to ±1° C. by means of two thermocouples calibrated before and after the anneals. Provision was made for rapid quenching by shattering the glass tubes in cold water; this was very necessary because if the glass failed to crack mercury would condense from the hot specimen onto the

TABLE 2.—*Composition by Synthesis, Time, and Temperature of Anneal, and Lattice Parameter of Silver-mercury Alloys Quenched from Temperature*

Alloy	Wt. Per Cent Hg	Anneal, Deg. C.	Time, Hr.	Lattice Parameter, Å
1A	10.01	270	600	4.0911
2A	20.00	270	600	4.1095
3A	30.00?	270	600	4.1289
4A	35.01	270	600	4.1378
5A	40.00	270	600	4.1577
6A	45.00	270	600	4.1635
7A	50.00	270	600	4.1750
8A	52.50	270	600	4.1830
9A	55.00	270	600	4.1829
10A	52.50	100	1000	4.1782
11A	55.00	100	2000	4.1793
12A	52.50	245	1000	4.1820
13A	55.00	245	1000	4.1823
14A	52.50	245	2000	4.1800[a]
15A	55.00	245	2000	4.1800[a]

[a] Poor quench. Aged two weeks at room temperature before X-raying.

TABLE 3.—*Lattice Parameters of Alloys 1A to 15A after Additional Treatment as Noted.*

ANALYSIS SHOWS COMPOSITION AFTER FINAL TREATMENT

Alloy	Condition	Anneal, Deg. C.	Time, Hr.	Lattice Parameter, Å.	Wt. Per Cent Hg
1A	Worked	270	500	4.0910	9.98
2A	Worked	270	500	4.1066	19.97
3A	Worked	270	500	4.1265	28.98
	Worked	270	+500	4.1263	
4A	Worked	270	500	4.1366	35.01
5A	Worked	270	500	4.1488	40.00
6A	Worked	270	500	4.1602	44.95
	Worked	270	+500	4.1605	
7A	Worked	270	500	4.1731	49.15
		186	+300	4.1730	
8A	Worked	270	500	4.1828	52.49
9A	Worked	270	500	4.1832	55.00
10A	100 anneal	245	300	4.1814[a]	52.50
8A	270 anneal	245	300	4.1818	52.49
12A	245 anneal	186	300	4.1810	52.50
11A	100 anneal	186	300	4.1811	55.00
14A	245 anneal	100	300	4.1805	52.50
15A	245 anneal	100	300	4.1805	55.00

[a] Uncertain quench.

cold glass, thereby changing the concentration in the surface layer, which is all that is measured by X-rays. The anneals at 100°, 186° and 245° were carried out by suspending the specimens in constant boiling flasks fitted with reflux condensers by means of ground-glass joints. For 186° aniline was used and for 245° di-ethylene glycol. In both cases the actual temperature was checked by accurate mercury thermometers with appropriate emergent-stem corrections.

The composition values shown in Table 3 were determined by analysis after final treatment, and it may be noted here that small discrepancies between these and the intended compositions can in all probability be attributed to the machining of specimens that were not homogeneous at the time.

Determination of Lattice Parameters and Solubility Limits

The method of determination of lattice parameters differed only in certain details from that described by Phillips and Brick.[8] Exposures were made in a semicircular Debye-Scherrer camera having a diameter of 6.25 in. With copper *K*-radiation from a Seeman demountable, hot-cathode tube operating at 40,000 volts and 25 milliamperes, exposure times varied from 3 to 4 hours.

It has been shown by Van Arkel[9] that for a reflection $\theta = 90°$ the error in lattice parameter becomes zero, and he has derived an error function permitting a convenient extrapolation, which, if used in connection with 83° to 89° reflections, renders negligible all errors other than those resulting from inaccuracies of film measurements. In a system in which the lattice constant undergoes such a marked change as in the alloys of silver and mercury, it is seldom possible to choose any one radiation to give reflections whose θ value is greater than 83° throughout the entire range of composition. Fortunately, in the present instance copper *K*-radiation yielded lines at reflecting angles greater than 85° throughout the range 49.1 to 52.2 per cent Hg. Since this included the upper end of the lattice constant-concentration curve as well as the entire variation of solubility with temperature, determinations were very accurate where they were most vital (Fig. 2*h*, *i*, *j*). The estimated error in the parameter values reported in the present investigation is from ±0.0001 to ±0.0005 Å., depending upon the position of the reflection circles.

Between pure silver and 20 per cent Hg, extrapolations were made from the $\{044\}K\beta$, through the $\{333\}K\alpha$ doublet; between 30 and 45 per cent Hg, from the $\{333\}K\alpha$ doublet through the $\{133\}K\beta$; and between 50 and 55 per cent Hg, from the $\{135\}K\beta$ through the $\{244\}K\beta$.

Lattice parameters corresponding to alloys that were given heat-treatments previously described are tabulated with the heat-treatments and compositions in Tables 2 and 3. The values listed in Table 3 are shown graphically in Fig. 3. The consistency of the points on the lattice

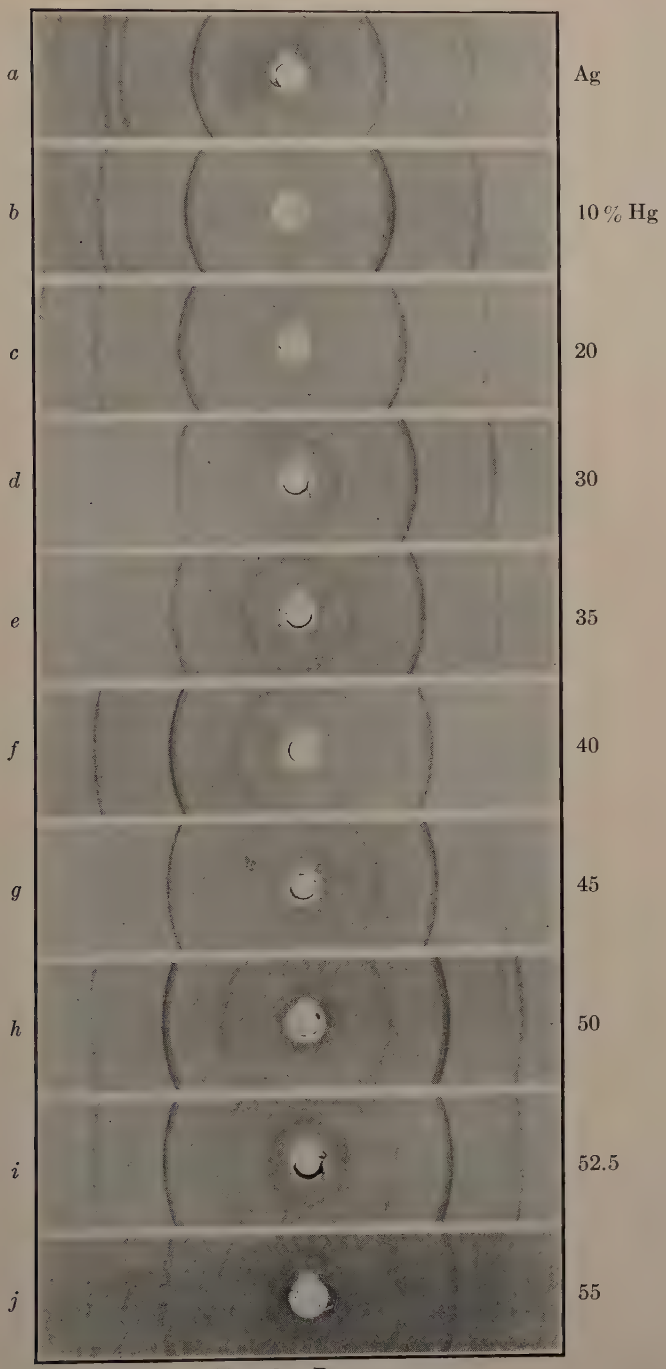

FIG. 2.—PHOTOGRAMS.

constant-concentration curve, as well as the sharpness of the photograms in Fig. 2, strongly suggest that a true state of equilibrium has been closely approached. That the gradual change in slope of the curve disagrees with Vegard's law is not disquieting in view of the fact that in some of the simplest systems, such as copper-silver and silver-gold where solvent and solute have the same valence and crystal structure, the lattice expansion or contraction is not given by a straight line. It might well be questioned that one should expect linearity of a function expressing the solution of such a large proportion (over 35 atomic per cent) of foreign atoms possessing a different crystal structure. Variations in lattice parameter were from 4.0774 Å., which was in good agreement with values of Owen and Yates,[10] to 4.0831 Å. for the saturated solution at 270°. The upper portion of the lattice constant-concentration curve is shown on an exaggerated scale in Fig. 4.

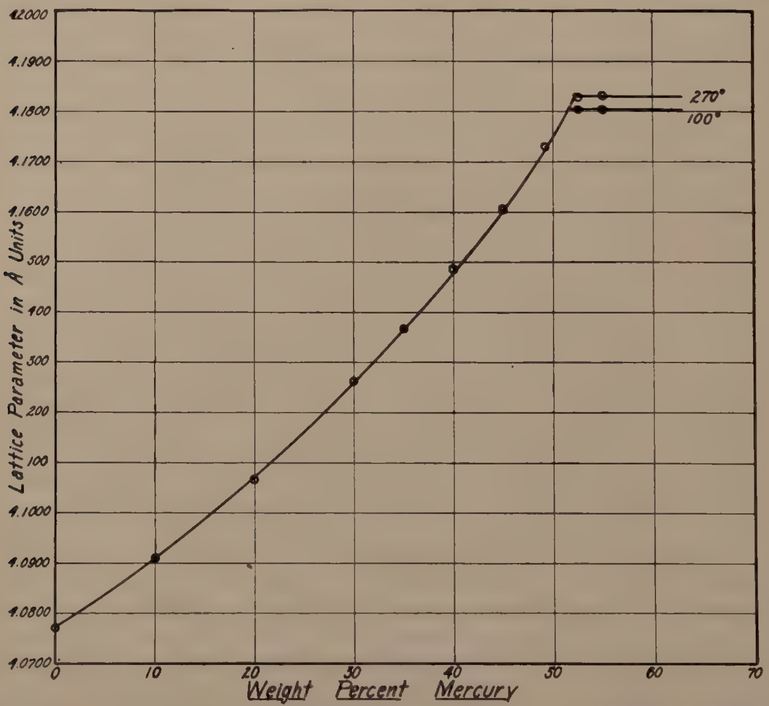

Fig. 3.—Change of silver lattice with increasing mercury content.

Tables 2 and 3 indicate all the heat-treatments carried out. Specimens 8A to 15A, which all had compositions of 52.5 or 55 per cent Hg, and were, therefore, in the two-phase field of alpha plus beta, were annealed and measured and then reannealed in such a way that equilibrium was approached from both sides. In some cases the specimen was reannealed at the same temperature for an additional period of time.

The column headed "condition" in Table 3 shows the previous treatment of that particular specimen.

In Fig. 4, the results of the measurements of alloys subjected to anneals below 270° are plotted. From this plot, the intersections of the annealing horizontals with the lattice constant-concentration curve give values for the limits of solid solubility at the various annealing temperatures. When these points are placed on the constitutional diagram, Fig. 5, a smooth curve can be drawn through them indicating a solubility of 52.4 per cent Hg at 276° C., which decreases at lower temperatures to a value of about 51.6 per cent Hg at 100° C. This is better illustrated by Fig. 6, in which the scale is exaggerated.

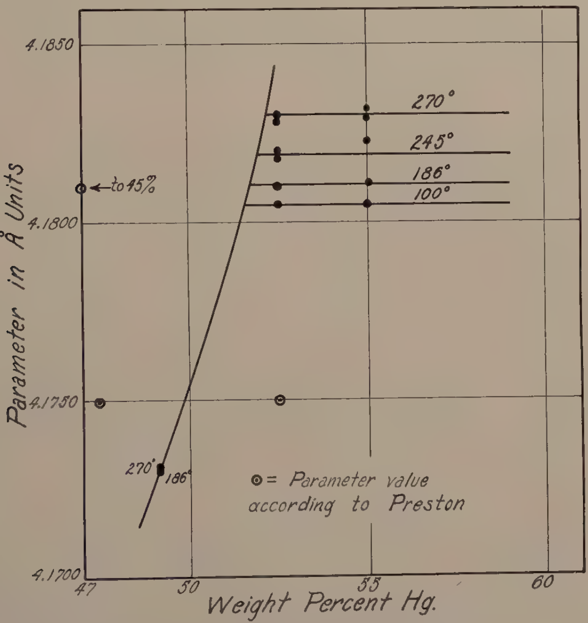

FIG. 4.—UPPER PORTION OF CURVE SHOWN IN FIG. 3. SCALE EXAGGERATED AND INTERMEDIATE ANNEALS PLOTTED.

X-RAY DETERMINATION OF SOLIDUS

In view of the 7 per cent difference between the maximum solubility estimated by Murphy and that found in this investigation, it was thought advisable to attempt to check the position of the solidus near its junction with the solid solubility curve. Obviously, there was little likelihood that in a limited amount of time Murphy's very careful microscopic investigation could be bettered. In casting about for a promising method, it occurred to us that an ordinary solubility determination by means of lattice parameters would yield the necessary data, provided certain precautions were taken. To the best of our knowledge, a similar investigation has never been reported in the literature, but it appears to be a good argument that no other assumptions need be made in justification of such a study than are made in the familiar procedure of quenching specimens from temperature and observing them microscopically for the appearance of chilled liquid. The assumption in both cases is that the rapid cooling of the alloy essentially preserves the equilibrium conditions that prevailed at the elevated temperature, at least with respect to the proportionate amount of the primary alpha solid solution. Likewise, it is assumed that diffusion is inhibited to such a degree at ordinary temperatures that no appreciable changes take place before observations can be made.

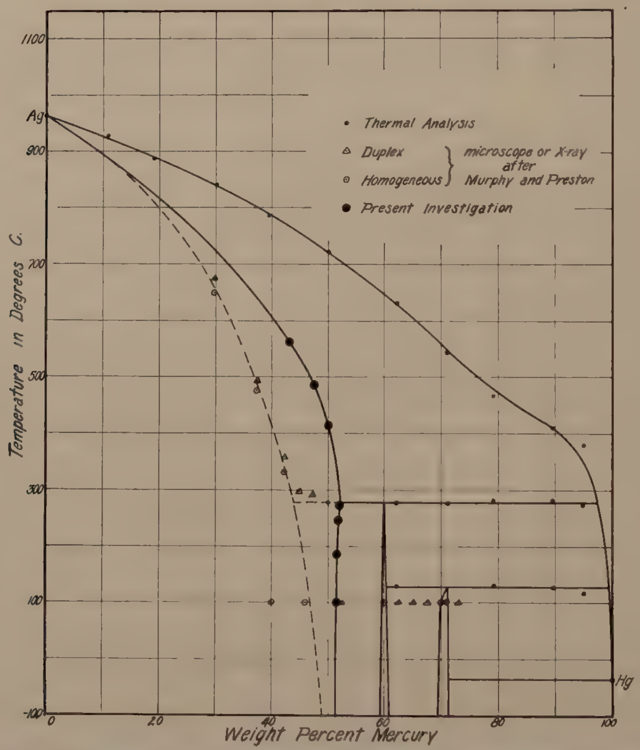

FIG. 5.—SHOWING RELATIONSHIP BETWEEN MURPHY'S DIAGRAM AND SOLIDUS AND SOLID SOLUBILITY CURVE INDICATED BY PRESENT INVESTIGATION.

Alloys with suitable compositions were selected from those which had been annealed to supposed equilibrium at the lower temperatures of the solid solubility investigation. The samples used at the different quenching temperatures are shown in Table 4, together with the lattice parameters observed. In the column headed "Source" the numbers 3A, 6A, etc. refer to Table 3, and indicate the previous heat-treatments of these specimens.

Needless to say, the composition of an alloy used for this determination had to be so chosen that the amount of liquid phase present at the quenching temperature was small, and it is interesting to note that if this were not done the specimen exploded to a powder when quenched. This was due to the sudden release of the pressure when the Pyrex container shattered; the internal pressure of the specimen was still at a high value of course.

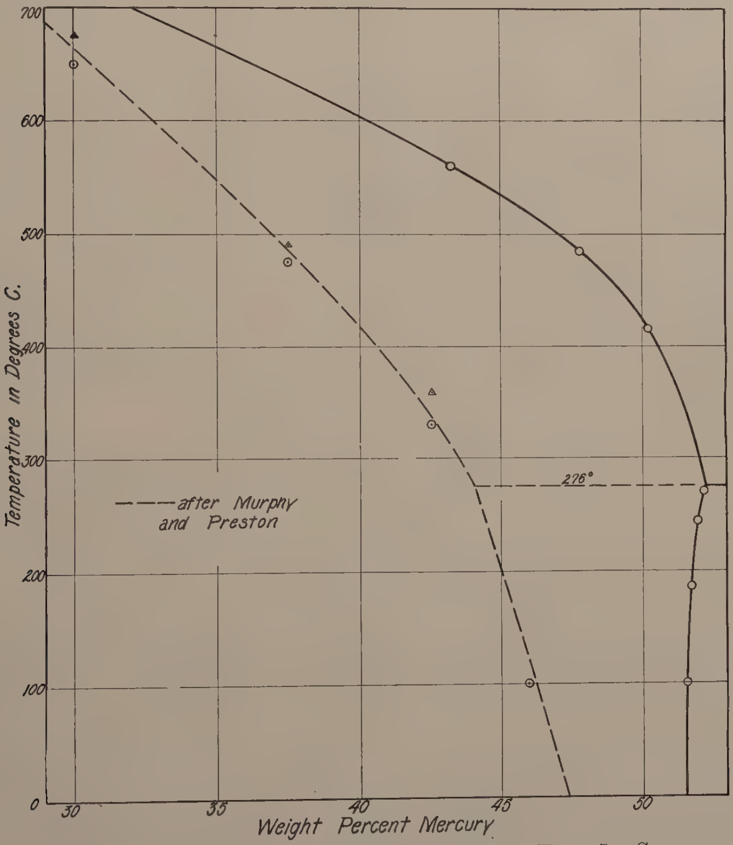

FIG. 6.—SOLIDUS AND SOLUBILITY CURVES SHOWN IN FIG. 5. SCALE GREATLY EXAGGERATED.

In a recent contribution, Brick, Phillips and Smith[11] reported appreciable differences in the parameter values of identical aluminum-manganese alloys, depending on their shape and size, hence upon strain incident to quenching. In order to make sure that this factor was not introducing errors into the present work, powders were prepared from two of our samples, given identical anneals and found to have lattice constants that checked well with the rod specimens. A more conclusive check was obtained in connection with the solidus determination. Alloy 3A

(30 per cent Hg), which had been originally annealed at 270°, was measured after each successively higher quench and found in each case to have a parameter value that checked well with the original. We concluded that quenching strains had a negligible effect in this investigation.

TABLE 4.—*Lattice Parameters of Alloys Quenched from Temperatures above the Peritectic Reaction Horizontal*

Alloy Mark	Wt. Per Cent Hg	Source	Anneal, Deg. C.	Lattice Parameter, Å.
1B	28.98	3A	416	4.1267
2B	44.95	6A	416	4.1606
3B	49.15	7A	416	4.1750
4B	55.00	9A	416	4.1754
1C	as above	1B	485	4.1263
2C		2B	485	4.1598
3C		3B	485	4.1694
4C		4B	485	4.1690[a]
1D		1C	560	4.1265
2D		2C	560	4.1557
3D		7A	560	4.1551[a]

[a] Alloy exploded upon quenching.

DISCUSSION OF RESULTS

All of the data are self-explanatory, and it is perhaps unnecessary to add a lengthy discussion. Apparently, they are consistent throughout. The sharpness of the X-ray patterns, the very long annealing periods, and the approach to equilibrium from both lower and higher temperatures indicate that the specimens measured were in a state of substantially true equilibrium, and that the curve obtained expressing the solubility of mercury in solid silver is the most accurate to date.

The only previous research with which these results need be compared is that of Murphy and Preston. Murphy obtained the solidus line, shown dotted in Figs. 5 and 6, by quenching alloys after one hour at temperature and determining microscopically the temperature at which the liquid phase appeared. Murphy himself expressed doubt concerning the finality of the solid solubility curve; also shown dotted in the same figures. He rejected his microscopic evidence in favor of X-ray determinations by Preston, who inferred from lattice-constant measurements that at 100° C. the solubility limit was 46 ±2 per cent Hg. The solubility curve was essentially determined by this point and one other, the intersection of the solidus with the peritectic horizontal.

Both Benedicks[12] and Hume-Rothery[7] have expressed their opinion that in all probability the slope of the solubility line is opposite to that in Murphy's diagram. As a possible criticism of the work, Hume-Rothery suggested that the alloys used by Murphy to determine the solidus might have been inhomogeneous and would, therefore, show melting of the mercury-rich metal at a temperature below that required under conditions of true equilibrium. Obviously, the effect of this would be to displace the intersection of the solidus and the reaction horizontal to the left. Murphy felt, however, that a preliminary 10-day anneal at 260° C., not mentioned in his paper, should have produced homogeneous specimens despite the fact that they were not deformed in order to hasten homogenization by recrystallization.

All the data in the present work seem to be in full support of the views expressed by Hume-Rothery. Apparently the discrepancy between our solubility limit at 100° and that estimated by Preston is not very serious. As a basis for his inference, he gives lattice-parameter values for alloys containing 45, 47.5, and 52.5 per cent Hg, all of which he considers to be saturated with mercury. These values, differing by 0.006 Å. and said by Preston to check within the experimental error, are plotted as dotted circles in Fig. 4. If an error of 0.006 Å. is referred to the lattice constant-concentration curve, it is found to correspond with a composition error of about 5 per cent. The conclusion is that the X-ray technique used by Preston was not well suited to the accurate determination of lattice parameters.

GOLD-MERCURY

Historically, the first studies of gold amalgams antedate most of the present methods of metallography, but, despite the many names that have since become associated with the constitutional investigation of this system, there remains some doubt concerning the form of the diagram. Hansen,[13] after a critical survey of the literature, has preferred the interpretation shown in Fig. 7. Values for the solid solubility of mercury in gold are meager and the determinations of different investigators are not in good agreement. Their individual results are shown graphically in Fig. 9.

Preparation of Alloys

The gold used in making the amalgams was examined spectrographically and found to contain silver in an unknown but very small quantity. As far as could be determined, no other impurities were present in measurable amounts. An attempt was made to further purify the gold by bubbling chlorine through the molten metal for one hour, but a subsequent spectrographic examination suggested that the silver remained in about the same concentration. Since the spectrograph is more sensitive to silver than to gold, it was estimated that silver was not present in quantities large enough to influence the results of the present investigation and no further purification was attempted.

The methods of preparing and heat-treating the gold-mercury alloys were similar to those already described for silver-mercury. Individual specimens of the following compositions were prepared: 5, 7.5, 10, 12.5, 15, 16, 17, 18, and 20 per cent Hg. In addition to these alloys, which were used to establish the lattice constant-concentration curve, a number of alloys were needed for long anneals at the different temperatures at which points on the solubility curve were desired.

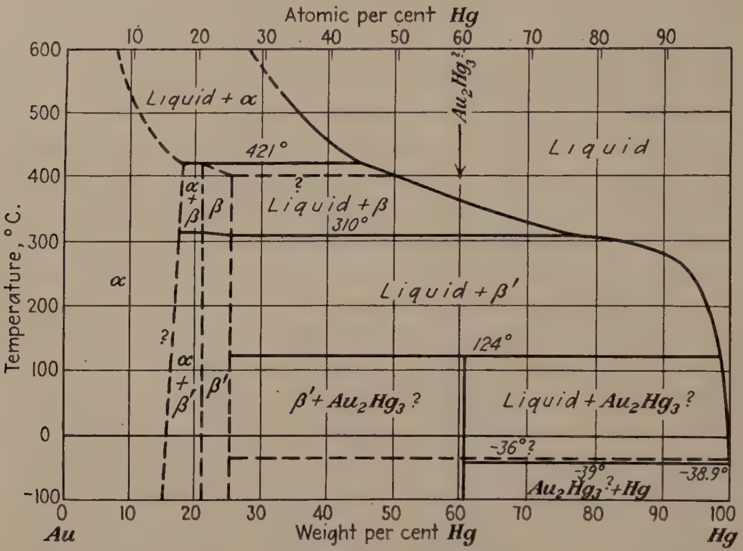

FIG. 7.—HANSEN'S INTERPRETATION.

TABLE 5.—*Indicating Composition, Annealing Time and Lattice Parameter of Specimens Used to Determine Lattice Constant-concentration Curve*

Mark	Wt. Per Cent Hg	Time, Hr.	Lattice Parameter, Å.
1	5.01	350	4.0838
2	7.48	350	4.0912
3	9.98	350	4.0971
4	12.53	350	4.1045
5	15.01	350	4.1083
6	15.98	350	4.1115
7	16.99	300	4.1142
8	18.00	325	4.1120
9	20.01	350	4.1180

Exactly the same technique was used in the heat-treatments of gold-mercury specimens as has been described in the previous section for those of silver-mercury. All alloys were given preliminary homogenization anneals at 400° C. for a period of two days, after which they were hammered to induce recrystallization, resealed in vacuo, and annealed at the desired temperature. The time and temperature of annealing to which each of the specimens was subjected are listed in Tables 5 and 6. It should be noted that in Table 5, specimens 1 to 9, used to determine the lattice constant-concentration curve, were not given a single anneal for the total time shown. After 200 hr. at temperature the specimens were quenched and X-rayed. When the X-ray photograms indicated that they were not homogeneous, they were hammered and returned to the anneal for the remainder of the indicated period.

TABLE 6.—*Indicating Composition, Time and Temperature of Anneal, and Lattice Parameter of Specimens Used to Determine Solubility Curve*

Mark	Wt. Per Cent Hg	Anneal, Deg. C.	Time, Hr.	Lattice Parameter, Å.
1A	18.00	390	300	4.1165
2A	20.01	390	300	4.1176
1B	18.00	320	380	4.1120
2B	20.01	320	380	4.1141
1C	18.00	300	300	4.1125
2C	20.01	300	300	4.1126
1D	18.00	245	720	4.1120
2D	20.01	245	720	4.1114
1E	18.00	186	740	4.1121
2E	20.01	186	740	4.1113
1F	18.00	100	770	4.1146
2F	20.01	100	770	4.1147

DETERMINATIONS OF LATTICE PARAMETERS AND SOLUBILITY LIMITS

X-ray technique used in the parameter measurements on the gold-mercury system was identical with that described for silver-mercury except that, for most specimens, nickel K-radiation was used instead of copper. When the lattice of the gold had been expanded close to the limit at the higher annealing temperatures, the interplanar spacing was suitable for copper K-radiation to give photograms that established the lattice constant with great accuracy. With the tube operating at 35,000 volts and 20 milliamperes, and using a nickel target, exposure times varied from 3 to 4 hours.

In the X-ray examination of the gold-mercury alloys using nickel radiation, the reflection circles measured were as follows: $\{224\}K\alpha_1$, reflecting at θ values from 80° to 85°: $\{224\}K\alpha_2$, from 81° to 86°; and $\{333\}K\beta_1$, from 71° to 73°. In the few examinations in which copper radiation could be used, the $\{135\}$ plane reflected the $K\beta_1$ radiation at θ values from 86° to 90°, and the $\{333\}K\alpha$ doublet reflected at angles of 76° to 77°. The corrected α_0 values were obtained by extrapolation for each photogram.

The lattice parameters obtained from measurements of the heat-treated alloys are shown with the corresponding values of composition and annealing temperatures in Table 5, and are represented graphically as a function of composition in Fig. 8. The relationship is almost linear, showing an expansion of the gold lattice from a cell dimension of 4.0699 to 4.1180 Å. at a concentration of 18.7 per cent Hg.

Table 6 lists the parameter values obtained from specimens that had been annealed at various temperatures. Since there is much disagreement concerning the significance of the thermal arrests in the gold-mercury system, it was thought that a reasonable number of well chosen points on the solubility curve might serve to clear up their interpretation. However, the parameter values obtained left much to be desired. Time did not permit an elimination of the discordant values by a repetition of the anneals and parameter measurements, therefore the highest values of the parameter were selected for each temperature, ascribing the lower value to either a faulty quench or a specimen too low in mercury to reach a saturation value at that temperature. By reference to the lattice constant-concentration curve, the solubility limits for the different temperatures were secured and are shown in Table 7. These are plotted against temperature in the exaggerated portion of the constitutional diagram reproduced in Fig. 9. The curve drawn through these points has an inflection at about 330° C. and then drops almost vertically with decreasing temperature. The maximum solubility is indicated to be about 18.75 per cent Hg at 421° C., and this falls off with decreasing temperature to about 15.7 per cent at ordinary temperatures.

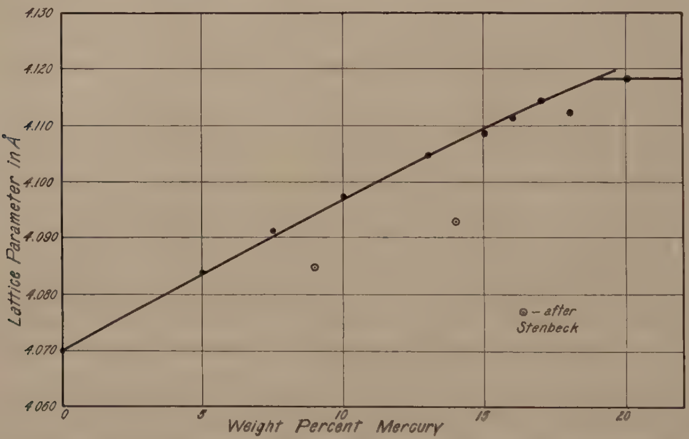

FIG. 8.—CHANGE OF LATTICE PARAMETER OF GOLD WITH INCREASING MERCURY CONTENT.

DISCUSSION OF RESULTS

A lengthy discussion of the data is unnecessary since a graphic representation is the best test of their significance. It is possible that the data with regard to the solubility at lower temperatures have been interpreted incorrectly and that there is an increase in the saturation limit below 200°C. However, until further evidence is available on this point,

TABLE 7.—*Compositions Corresponding to Observed Lattice Parameters at Various Temperatures*

Annealing Temperature, Deg. C.	Lattice Parameter, Å.	Wt. Per Cent Hg	Annealing Temperature, Deg. C.	Lattice Parameter, Å.	Wt. Per Cent Hg
416	4.1180	18.7	245	4.1120	16.0
390	4.1176	18.5	186	4.1121	16.1
320	4.1141	17.1	100	4.1147	17.2
300	4.1126	16.3			

the curve shown in Fig. 9 appears to be the more likely. The high parameter values obtained from the specimens annealed at 100° could be explained by incomplete precipitation from the supersaturated solution remaining from the preliminary 400° anneal. This is difficult to understand, because, from the appearance of the photograms, the specimens had obviously recrystallized following their deformation by hammering.

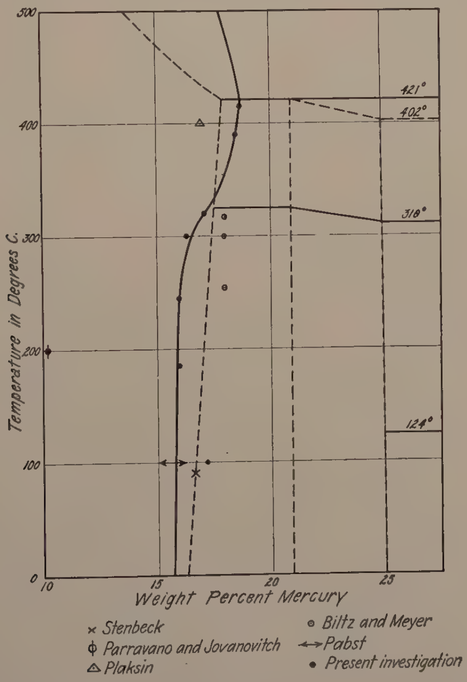

FIG. 9.—SOLID SOLUBILITY DATA ON THE SYSTEM GOLD-MERCURY.

That the data seem to indicate an inflection in the solubility curve seems reasonable. It is not an unnatural phenomenon, having been observed in the systems copper-germanium and copper-antimony, and attributed to a change in that phase with which the saturated solid solution is in equilibrium. As drawn in Fig. 9, the inflection occurs just above the thermal arrest interpreted by Anderson[14] and Hansen[13] to indicate a polymorphic transformation in the beta phase.

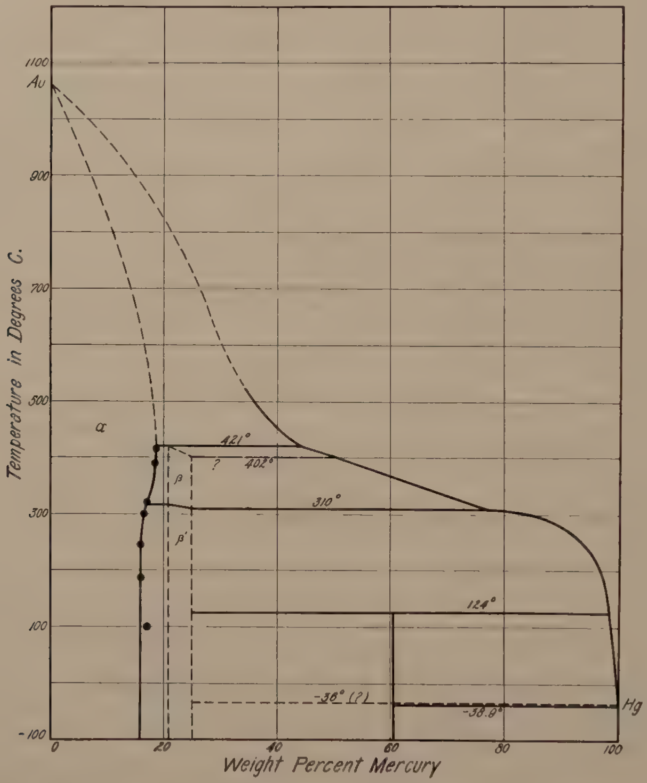

FIG. 10.—MOST PROBABLE FORM OF GOLD-MERCURY CONSTITUTIONAL DIAGRAM (1937).

The results of all previous investigators are included for comparison in Fig. 9. Since, with the exception of the three values of Biltz and Meyer, all workers have reported single points that are not in agreement with one other, a comparison of the present data with those of other investigators is not significant. One point that we are at a loss to explain is the marked discrepancy between the lattice-parameter values found by Stenbeck and those obtained in the present work. To show this more clearly, the two values reported by Stenbeck are plotted in Fig. 8. Even more puzzling is the fact that the solubility value deduced by him does not differ markedly from ours. It would be interesting to learn the exact reason for this disagreement, but for the present it is somewhat reassuring to note that our results represent a greater change in lattice parameter and, therefore, a more probable expression of equilibrium.

While no claim of finality is made for the data presented here, it is felt that they represent the most accurate criteria available at this time for the establishment of the solid solubility curve. The most probable approximation to the true form of the constitutional diagram of the system gold-mercury is shown in Fig. 10.

SUMMARY

Using a back-reflection method of X-ray analysis, the limits of solid solubility of mercury in silver have been established over the temperature range, 100° to 276° C. From the maximum value of 52.4 per cent Hg at 276°, the solubility falls gradually to 51.6 per cent at 100°.

The application of similar technique to the system gold-mercury over the temperature range 100° to 421° indicated that the solubility of mercury in gold attains a maximum value of 18.75 per cent Hg at 421°. The solubility falls off rapidly as the temperature decreases to 300° and then falls very slowly to 15.7 per cent at 100°. The curve is characterized by an inflection at about 330°.

X-rays have also been applied in the determination of the solidus curve for the system silver-mercury, in the temperature range 276° to 560°. The results are in good adjustment with the solubility data.

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DISCUSSION

(Frederic E. Carter presiding)

E. R. Jette,* New York, N. Y.—There are several interesting points upon which I should like to comment. The first one is the authors' use of Vegard's law and the way their results are plotted. Vegard's law applies only to cases of atomic substitution, therefore the proper composition unit for plotting and determining whether there are any marked deviations or not is in atomic per cent rather than weight per cent. If the results in Table 3 are recalculated to atomic per cent, the deviation is comparatively small; at about half the distance between the two ends of the lattice-parameter curve in Fig. 3, the difference is only about 0.004 Å. from the linear relation.

I want to compliment the authors on the use of the X-ray method for determining the solidus. All those who have experimented with this type of investigation will realize that it is a method that works when it works; that is, there is no predicting ahead of time whether this particular type of method will serve or not, since it depends very much on the rates of the transformations that take place during the quenching. As a matter of fact, Mr. Foote and I have used much the same idea in trying to determine the solubility of nickel in alpha iron.[17] We used practically the same technique as Day and Mathewson in selecting an alloy and then finding a temperature at which there was not too much of the gamma phase present, instead of the liquid phase as in the present investigation. We found that if there was too much of the gamma phase present, the results were bad and a lower temperature had to be used.

One other point of theoretical interest, especially in connection with another paper[18] presented, concerns the solubility limits. Hume-Rothery and his school, and also a group of theoretical physicists, have laid much stress on the ratio of the number of electrons to the number of atoms in lattice, or what is known as the electron concentration. For alloys of copper or silver with quite a number of other elements, they found that the maximum solubility gave an electron concentration of about 1.4. This quantity is calculated simply by taking the atomic fraction times the valence and adding the results for the two elements. Certain theoretical treatments have also given the same limit of 1.4.

The silver-mercury system that Day and Mathewson have investigated gives an atomic solubility of 37.5 per cent mercury and silver, which gives an electron concentration of 1.38, which is in satisfactory agreement with the theory.

In the gold-mercury system, the atomic solubility is only about 18.5, and the electron concentration comes out only 1.2, approximately, which is very far off for that kind of ratio.

Considerable importance has been placed on the alloys of copper and silver. In the theoretical developments it is rather important to see that in both this paper and the one by Coffinberry and Hultgren there are serious deviations from the theoretical results for the gold alloys, which, for other reasons, might be considered as similar to those of copper and silver.

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* Associate Professor of Metallurgy, Columbia University.

[17] E. R. Jette and F. Foote: *Trans.* A.I.M.E. (1936) **120**, 259.

[18] Coffinberry and Hultgren, page 249 this volume.

F. E. Carter,* Newark N. J.—On reading the Murphy and Preston papers[19] one notes the general acclaim that was given to the way in which the authors had overcome the experimental difficulties. I think the present authors are also to be congratulated on handling a difficult problem very successfully. There are certain small changes from previous work, and I presume those are chiefly because in this present paper the alloys were made thoroughly homogeneous. It seems to me that much work has been done up to the present time in which the experimenters have not taken into full consideration the possibility that the materials they were working with were not thoroughly homogeneous.

R. Hultgren.—Professor Jette has noted that in two of the three systems presented today the maximum electron concentration in the alpha phase falls below the value 1.4 electrons per atom permitted by theory. I do not believe this result is in contradiction to theory, which merely fixes an upper limit to solubilities. Smaller solubilities can be due to other factors, hence these are negative results. In regard to gold-aluminum, we have suggested that the small solubility may be due to exceptional stability of the beta prime phase.

H. M. Day (written discussion).—In drawing conclusions concerning the linearity of the lattice-parameter function, the composition should, of course, be considered in atomic per cent. However, this conversion does not alter the consistent divergence from linearity but only the relative departure in Ångström units.

Since the preparation of this paper, I have reread a paper written by A. Pabst, who examined the gold-mercury system by means of X-rays in 1929. I discovered a table of lattice parameters that had been overlooked in my first survey of his work. It is somewhat reassuring to note that their values check our data closer than their admitted experimental error.

Professor Jette has discussed the electron concentrations that correspond to the solubility limits in the systems gold-mercury and gold-aluminum. As he has pointed out, the marked discrepancies between the observed values and the predicted value of 1.4 are of theoretical interest but do not represent a legitimate criticism of the solubility values. Dr. Hultgren has stated that the electron concentration of 1.4 predicts only the maximum solubility and the actual limit is very sensitive to other factors such as the atomic size factor and electronegative valency effect. It would be interesting to know what factor is operative in the system gold-mercury, because the size factors here and in the silver-mercury system are equally favorable. Of one thing, however, we may be reasonably certain. The disagreement between observed and theoretical electron concentrations cannot be attributed to an error of 20 atomic per cent in the solubility limit.

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[19] See references, page 279.

Properties of the Platinum Metals, II—Tensile Strengths of Platinum, Palladium and Several of Their Commercial Alloys at Elevated Temperatures, with a Few Notes on High-temperature Corrosion Resistance of Platinum

By E. M. Wise* and J. T. Eash,† Members A.I.M.E.

(New York Meeting, February, 1938)

Many of the platinum metal alloys are hot-forged in the early stages of reduction from ingot and substantial quantities of platinum alloys are commercially employed at very high temperatures in ammonia oxidation units, orifices for forming glass rods and fibers and as cathodes in long-life thermionic amplifiers. They are used also for electrical heating resistors, safety blowout disks, thermocouples and crucibles. The tensile properties at elevated temperatures are important in many of these situations but data on the subject are limited. Creep data also are important, but will not be covered at this time.

Scope and Conclusions

Tensile tests were carried out at room temperature and elevated temperatures up to 1100° C. on previously well annealed samples of platinum, palladium and several of their important alloys with compositions shown in Table 1. The results are presented graphically in Figs. 1 to 4.

The tensile strengths of platinum and the platinum-base alloys (with the exception of the 10 per cent rhodium-platinum alloy) at 1100° C. are from 16.6 to 18.8 per cent of the strengths of the same alloys (well annealed) at room temperature. The strength ratio of the 10 per cent rhodium-platinum alloy is 22.3 per cent, which is appreciably higher than that of the other materials tested.

The tensile strengths of palladium and the palladium alloy at 1100° C. are from 10 to 11.2 per cent of the room-temperature values.

The elongations of platinum and its alloys tend to increase at temperatures above 600° to 800° C., while the two samples of pure palladium show a maximum at 600° C.

Manuscript received at the office of the Institute Dec. 1, 1938.

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The effect of alternately oxidizing and reducing atmospheres on certain alloys is discussed and data on the notable resistance of platinum to SO_2 and H_2S at high temperatures are presented.

TABLE 1.—*Compositions of Samples Tested*[a]

Sample	Weight, Per Cent					
	Pt	Pd	Ir	Rh	Ru	Ni
C.P. platinum	99.9+					
No. 1 platinum	99.9					
5 per cent Ir Pt	95		5 ± 0.1			
10 per cent Rh Pt	90			10 ± 0.1		
5 per cent Rh, 20 per cent Pd Pt	75	20 ± 0.2		5 ± 0.1		
5 per cent Ni Pt	95					4.5–5
No. 1 palladium		99.9				
Palladium (C)		99.9				
1 per cent Rh, 4 per cent Ru Pd		95		1	4	

[a] All samples were supplied in wire form by Baker & Co. and represent commercial products.

CHARACTERISTICS OF THE ALLOYS AND EXPERIMENTAL PROCEDURE

The annealing characteristics of most of these alloys, from the same heats, were studied in a previous communication.[1] The palladium sample C was not dealt with in the earlier paper and while its chemical purity was at least as high as the commercial No. 1 palladium, its annealing temperature and hardness were slightly higher than the No. 1 sample; which may have been due to the presence of finely dispersed inclusions.

The samples employed in the present tests were 0.050-in. wire that had been annealed for 5 min. at 1100° C. in a gas furnace. The high temperature and slightly reducing atmosphere employed in this preliminary anneal (applied to alloys that probably had been previously annealed under oxidizing conditions) were not entirely appropriate for some of the alloys and yielded a rather large grain in the unalloyed samples and in some instances produced some slight surface deterioration, which doubtless reduced the elongation and reduction of area but probably had little effect on the tensile strength.

The samples were 8 in. long and were heated in a 6-in. electric resistance furnace containing a heavy-walled nickel tube to minimize the temperature gradient, which was not over 5° C. at 1100° C. over the significant portion. The small wires were held in clamps external to the furnace to minimize the loss of heat from the furnace. Temperatures below 600° C. were measured with small base-metal couples while at the higher temperatures a noble platinum-rhodium platinum couple was used. The wires were held at temperature for 5 min. prior to testing, except at 200° C., where 7 min. was employed, and were then pulled with a head speed of 0.5 in. per minute. An Amsler testing machine was used, in which appreciable movement of the "fixed" head occurs during straining and consequently the actual rate of strain is below the average value until maximum load is attained and above the average thereafter.

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[1] References are at the end of the paper.

Light gauge marks were applied to the specimen to mark the 2-in. gauge length and the reduction of area was estimated by projecting a shadow of the wire on a screen at 25 diameters. Where the reductions were extremely high, in a few instances it was difficult to be entirely certain of the portion involved in the final break, but on the whole the method was quite satisfactory.

Results and Discussion

The observed tensile data for platinum and its alloys are shown in Figs. 1 and 2 and corresponding data for palladium and one of its alloys in Fig. 3.

The strength vs. temperature relation for the C.P. platinum is a smooth curve, which falls from 20,700 lb. per sq. in. at room temperature to 3400 lb. per sq. in. at 1100° C. The strength of the No. 1 platinum is slightly higher than that of the purer sample but closely approaches the latter at 1000° and 1100° C. It may be remarked that recent improvements in processing, largely in melting technique, have led to the production of even softer platinum than the C.P. sample tested, tensile values of the order of 17,000 lb. per sq. in. at room temperature having been observed by C. S. Sivil.

The hardened platinums containing 5 per cent Ir, 10 per cent Rh and 5 per cent Rh plus 20 per cent Pd show an appreciable drop in strength at 200° C. followed by a more gradual fall to 800° C. The strength of the 10 per cent Rh alloy falls more slowly than the others at temperatures above 800° C. and at temperatures above 1100° C. is undoubtedly the strongest of the alloys tested. The 5 per cent nickel-platinum alloy shows a relatively small drop in strength up to 400° C. but the strength falls steadily thereafter, becoming equal to that of the initially less strong 10 per cent rhodium-platinum alloy at 1100° C. The shape of the strength-temperature curve might suggest a mild precipitation effect at about 400° C.

The elongations of the nearly pure platinums are somewhat erratic, probably because of the large grain size resulting from the high anneal, but on the whole, increase at temperatures above 600° to 800° C. The alloyed platinums tend to yield slightly lower elongations at temperatures up to 400° C. but increase in elongation at higher temperatures. The behavior of the 5 per cent nickel platinum at 1000° C. appears to arise from surface checking.

The reduction of area is generally above 80 per cent and, with the exception of the 5 per cent nickel-platinum alloy, shows a general tendency to increase with temperature. The drop in the reduction of area of the 5 per cent nickel-platinum alloy probably arises from surface chocking and is believed not to be typical of the alloy but to arise from

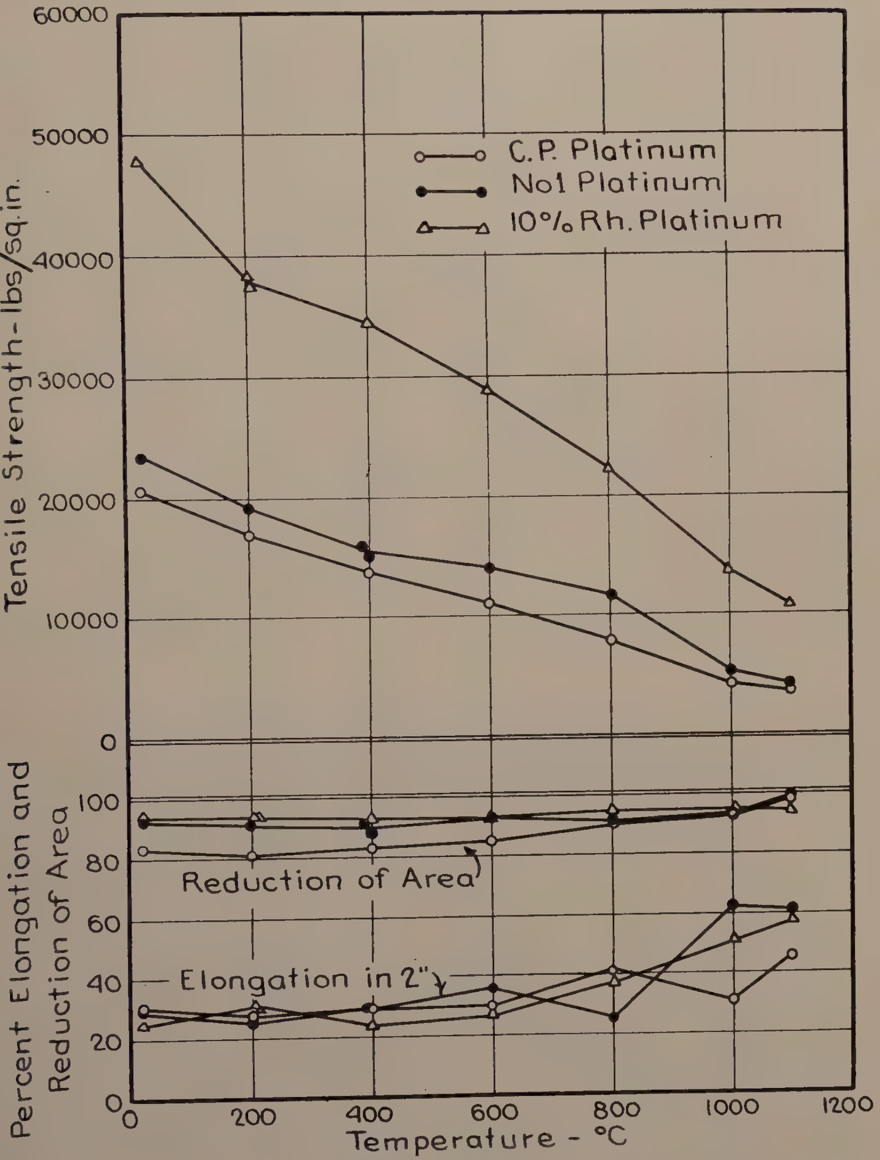

Fig. 1.—Tensile data for platinum and its alloys.

the effects of the previous annealing treatment and perhaps to some oxidation during the hot tensile test itself.

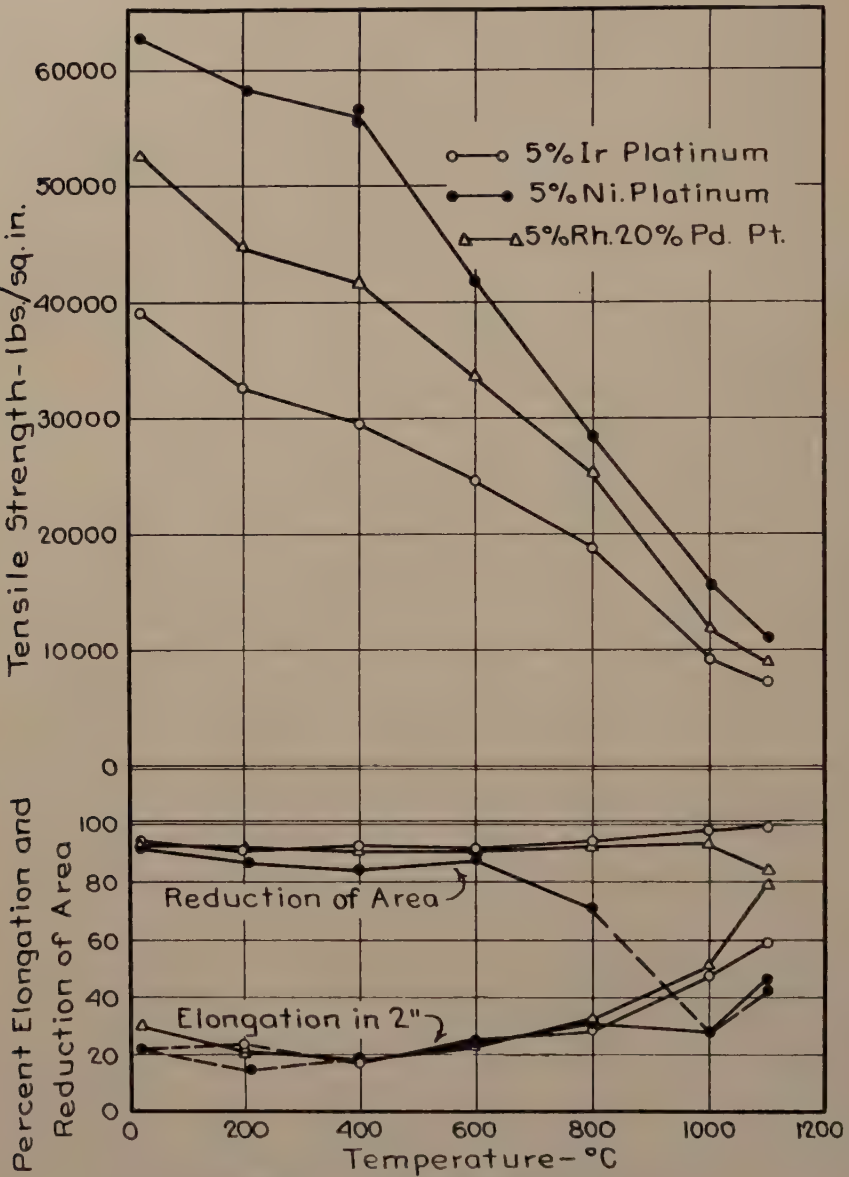

FIG. 2.—TENSILE DATA FOR PLATINUM AND ITS ALLOYS.

The strengths of the No. 1 palladium and palladium C are about 28,000 lb. per sq. in. at room temperatures—considerably above the values for platinum and fall smoothly but more rapidly than C.P. and

No. 1 platinum as the temperature is increased, so that at the higher temperatures the strength of palladium is slightly below that of platinum.

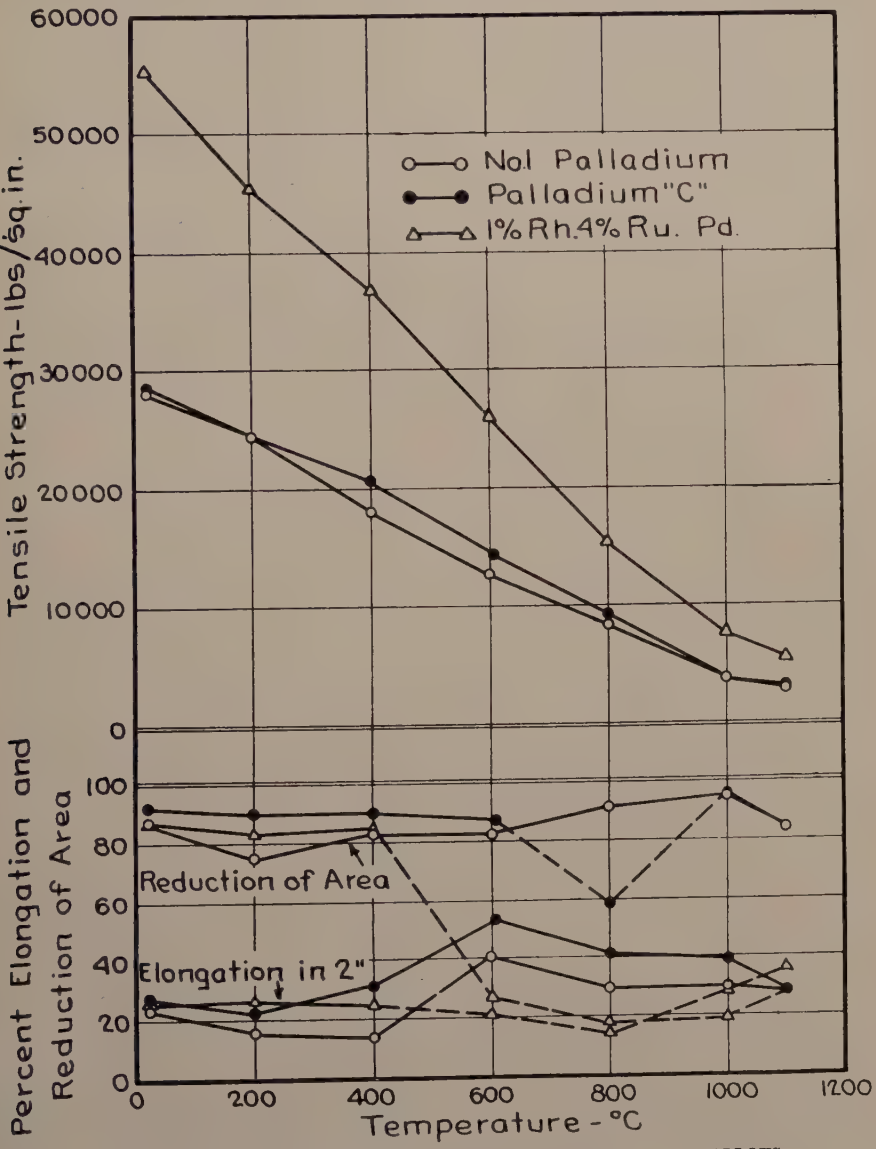

FIG. 3.—TENSILE DATA FOR PALLADIUM AND ONE OF ITS ALLOYS.

The 1 per cent Rh 4 per cent Ru hardened palladium has a room-temperature strength of about 55,000 lb. per sq. in. but its strength falls more rapidly than the hardened platinums and the alloy is softer than the 5 per cent iridium platinum at 700° C. and above.

The elongations of the two palladium samples attain a sharp peak at 600° C. for reasons that are not clearly evident. The rhodium-ruthenium hardened palladium shows a minimum elongation of 13 per cent at 800° C. but an increase at higher temperatures despite some surface checking. The reduction in area of this alloy shows a marked drop above 400° C. The reduction in area of the pure palladiums shows no

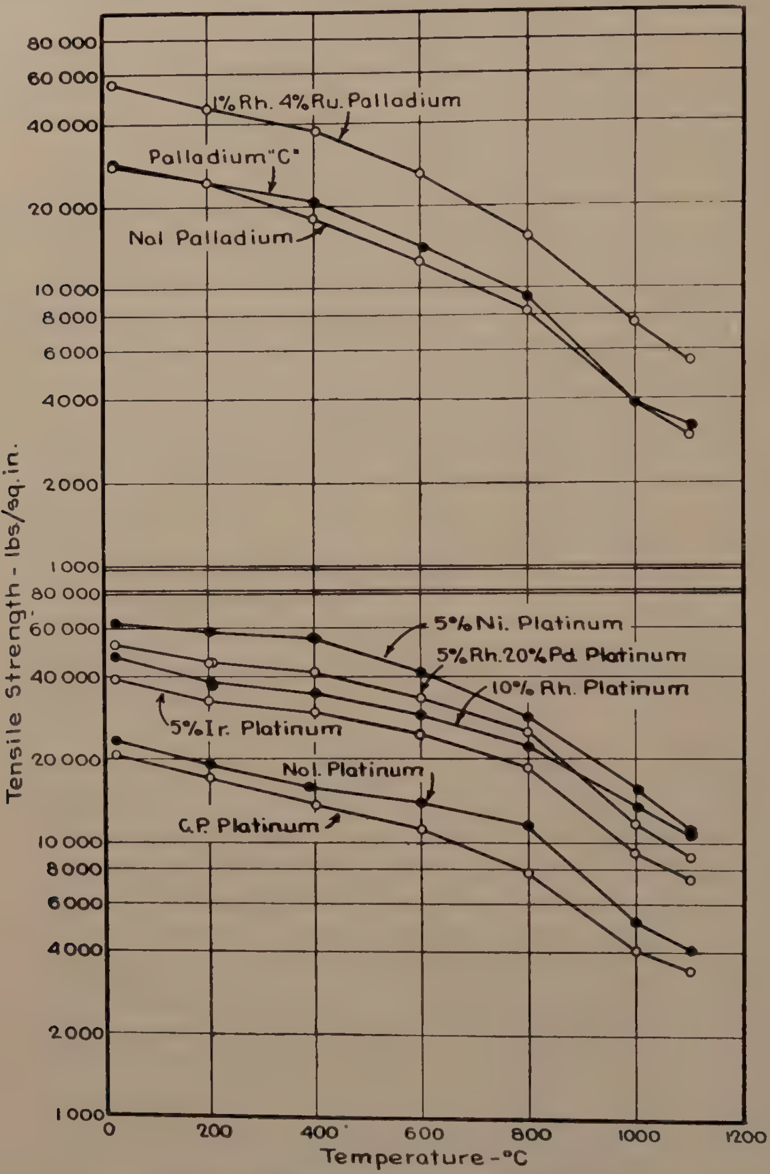

Fig. 4.—Ultimate strength of alloys.

systematic trend with temperature—the drop at 800° C. being associated with surface checking.

The ultimate strengths of all the alloys are plotted logarithmically against a linear temperature scale in Fig. 4. It will be noted that the shapes of the strength-temperature curves of the platinum series are similar in character, except for their vertical displacement, although at temperatures above 800° C. the strength of the 10 per cent Rh alloy falls less rapidly than do the other materials. Aside from this it appears that the relative strengthening effect of the several hardeners is approximately the same over the range of temperature and alloys studied. The strength of palladium falls a little more rapidly than platinum and this is also shown by the single hardened palladium alloy tested.

These conclusions apply to previously annealed wire and would not be expected to be equally valid for initially cold-worked materials possessing different annealing temperatures.

PREVIOUS WORK

Jedele,[2] in an investigation of the effect of alloying phosphorus and sulphur with platinum and palladium, ran tensile tests at both room temperature and 850° C. on some of the samples. The data in Table 2 were obtained on small rods generally annealed at 850° C. His results on the tensile strength of pure platinum and palladium agree well with

TABLE 2.—*Tensile Data on Small Rods Annealed at 850° C.*

Per Cent P	Per Cent S	Room Temperature		850° C.	
		Ultimate, Lb. per Sq. In.	Elongation, Per Cent	Ultimate, Lb. per Sq. In.	Elongation, Per Cent
		Platinum			
0.000	.....	21,050	27.1	9,800	9.0
0.001		21,200	24.9	11,200	6.1
0.003		19,800	14.2	5,970	6.2
	0.005	21,800	24.7	7,500	14.5
	0.02	23,200	26.2	10,500	14.0
	0.06	23,600	10.1	9,800	5.5
	0.15	28,300	14.7	12,400	5.8
		Palladium			
0.000		31,800	23.1	7,500	9.2
0.006		34,000	23.4	5,800	15.0
	0.001	27,600	24.2	9,300	16.8
	0.003	29,300	26.5	11,500	18.8

those reported herein, but the elongation values at high temperatures are lower, probably because of different experimental conditions.

EFFECT OF HEATING ATMOSPHERE ON SOME OF THE ALLOYS

The cause of the surface checking noticed in several of these tests is not entirely known, but it has been found that where the annealing atmosphere was oxidizing and then reducing rather severe surface damage and blistering can arise with certain metals and alloys. This damage is apparently due to the presence of oxygen in solid solution which in a subsequent treatment in a hydrogen content reducing atmosphere reacts to form water vapor, which causes blisters and weakens the grain boundaries. This has been noticed with silver, palladium-silver alloys and to a slight extent with palladium, and is probably quite a general type of behavior, but is easily avoided by maintaining a constant atmosphere during the anneal. Platinum is not susceptible to this damage, however, as it is only slightly etched by the annealing treatments in oxidizing and reducing atmospheres, although in the presence of carbon or reducible substances damage may result.

Pure platinum and the 10 per cent rhodium-platinum alloy used for electric furnaces, thermocouples, ammonia oxidation catalysts and glass-forming equipment, as well as the 3.5 per cent Rh crucible platinum appear to withstand indefinitely prolonged high-temperature exposure without embrittlement unless contaminated and are the metals most generally applicable for general use at high temperatures. The 20 per cent rhodium-platinum alloy, which has found some application to electric-furnace windings, owing to its higher melting point and resistivity, becomes somewhat brittle on long heating although not sufficient to preclude its use for this particular purpose.

High-iridium-content platinum alloys and the base-metal hardened platinums ordinarily would not be employed for high-temperature service under oxidizing conditions but in the absence of oxygen as in vacuum tubes, fine filaments of the 5 per cent nickel-platinum operate at temperatures of the order of 750° C. for 50,000 hr. or more.

Even sulphurous atmospheres, the arch enemy of hot metals, are well tolerated by platinum at high temperatures. Sulphur dioxide has no more effect on platinum at elevated temperatures (up to 1000° C. to 1100° C.) than air. Platinum is very slightly attacked by hydrogen sulphide, acquiring a thin blue film. However, the film appears to be protective and there is no evidence of intergranular penetration or embrittlement.

The results of a limited group of tests on the resistance of pure platinum sheet to sulphur dioxide and to hydrogen sulphide are listed in Table 3. The data relate to the behavior of pure platinum strips heated in sulphur dioxide or hydrogen sulphide at the temperatures and times indicated.

TABLE 3.—*Corrosion of Pure Platinum*

Temperature, Deg. C.	Time, Hr.	Weight Change, Grams per Sq. Dm. in Test Period	
		SO_2	H_2S
800	1	Unchanged	+0.0128
1000	1	−0.0013	+0.0174
1000	12[a]		+0.024
1100	1[a]		+0.0031

[a] Cooled in 93 per cent N_2 7 per cent H_2, remainder cooled in air.

The exposed samples were subsequently subjected to bend tests at 1000° C. in air and found to be undamaged by the exposure to the sulphurous gases. The slight film formed on exposing platinum to hot hydrogen sulphide is readily decomposed in air at temperatures above about 600° C.

It should be noted that the rates of film formation in H_2S decrease with time, so that the effective corrosion rate per hour for long exposures will be much less than that indicated in Table 3. This is demonstrated by the fact that 12-hr. exposure results in a weight change little above that developed in a 1-hr. exposure.

For comparison with these low weight changes, it is interesting to consider the behavior of the base-metal alloys used under sulphurous

TABLE 4.—*Corrosion of Heat-resisting Alloys*

Weight Change Grams per Sq. Dm. in 1-hr. Test

Composition, Per Cent			Attack by H_2S			
Cr	Ni	Fe	At 900° C.	At 950° C.	At 1000° C.	At 1100° C.
20.4		Bal.		+12.0	+14.8	+25.3
30.79		Bal.		+ 9.8		+23.5
28	20	Bal.		+ 9.7		
28	25	Bal.			+11.7	+19.5
28	19	Bal.		+10.0	+12.4	+22.0
			Attack by SO_2			
20.4		Bal.	+0.008		+0.02 +0.05	
22	22	Bal.	+0.006 +0.018		+0.011	
28	26	Bal.	800° C. +0.006		+0.039	1200° C. +0.134

conditions. The data presented in Table 4, determined by J. T. Gow, show that the rates of attack of the resistant base-metal alloys by H_2S are of the order of 1000 times those observed with platinum under similar test conditions.

ACKNOWLEDGMENTS

The authors want to express their thanks to Paul D. Merica and A. J. Wadhams, Vice-presidents of The International Nickel Co., Inc., for their support in this work, to F. E. Carter and C. S. Sivil of Baker & Co., for their cooperation in preparing the materials tested, and to their own associates, R. Vines and R. H. Schaefer, for assistance in various phases of the work.

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DISCUSSION

(*Frederic E. Carter presiding*)

F. E. CARTER,* Newark, N. J.—It is pleasant to know that among the early metals to be studied at elevated temperatures is the platinum group. It is natural that the platinum metals and their alloys should be studied because they are chiefly used at high temperatures, and as Mr. Wise has said, in certain important industrial uses the platinum alloys have to retain their strength as well as possible.

Mr. Wise gives the tensile strengths of platinum and the platinum alloys in general at 1100° C. as from 16.6 to 18.8 per cent of the tensile strength at ordinary temperature, rhodium-platinum being a slight exception, or an important exception, in that it is 22.3 per cent. Palladium alloys fall in strength at that temperature to about 10 to 11.2 per cent of the strength at atmospheric temperature.

I should like to know what happens with other alloys, like the base metals. What percentage of the tensile-strength atmospheric temperature is retained at, say, 1000° C?

E. M. WISE.—Regarding the effect of temperature upon other metals, I might say that the tensile strength of commercial nickel at 1775° F. is 9.8 per cent of the room-temperature value, while that of Inconel (14 per cent Cr, 6 per cent Fe, remainder Ni) is 14 per cent of the room-temperature value.

C. ZAPFFE, JR.,† Cambridge, Mass.—You have the two palladiums listed as having the same degree of purity. Have you any reason to offer why the properties should differ?

E. M. WISE.—In these tests, they do not differ very much. The annealing characteristics actually differ more than would be inferred from these high-temperature results. The difference probably lies in the presence of fine dispersion of perhaps silicate, or something of that sort, rising from melting conditions.

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* Physical Metallurgist, Baker & Co., Inc.

† Graduate Student, Harvard University.

C. Zapffe, Jr.—Did you find that it had reacted with silica? How did you melt it down?

C. S. Sivil,* Newark, N. J.—It was melted in lime.

E. M. Wise.—Have you any explanation as to the difference between the two?

C. S. Sivil.—None whatever. I was going to ask you about it.

E. M. Wise.—The most outstanding difference is shown up in some earlier work we did on the annealing characteristics, and it did appear as though there was something present restraining grain growth that led to a little abnormality in the recrystallization.

F. E. Carter.—The gas content?

E. M. Wise.—I do not think so, but I believe the difference to be due to dispersed oxide inclusions.

C. Zapffe, Jr.—There is apt to be trouble with adsorbed gas in palladium alloys. Have you tried to associate the peaks that you find in the elongation curves at 600° with the hydrogen content?

E. M. Wise.—No. In our early work on annealing we did investigate to some extent the effect of hydrogen on the tensile strength. I am certain that no hydrogen was involved in these particular tests. Hydrogen diffuses in and out very rapidly. As a matter of fact, if the material is allowed to cool in hydrogen, even quite rapidly, sufficient hydrogen is picked up to modify the tensile properties.

H. E. Stauss,* Newark, N. J.—We have been interested in the problem of tensile strengths of platinum alloys at high temperatures, but we have made our measurements on fine wires three-thousandths of an inch in diameter because of their immediate practical value. Of course there are difficulties in working with very fine wires, but there are compensating advantages. Not so much metal is needed. And, if a tensile-strength machine cannot be tied up for the experiments, it is possible to construct one's own equipment, which is what we have done.

We have worked with alloy series rather than with individual alloys. Using platinum alloyed with 20 per cent or less of rhodium, iridium or ruthenium, together with some ternary alloys of 80 per cent platinum or more, we found our results to lead to the general rule: The order of tensile strengths of a group of alloys is the same at temperatures up to 1000° C. that it is at room temperature; that is, of two alloys, the one that is stronger at room temperature is stronger at the higher temperature. It should be noted that in all our alloys the melting points were substantially the same and were large in comparison with the temperature range of the tests.

C. S. Sivil.—In a good deal of work that I have done, I have observed this variation of grain size in platinum alloys, but have not observed any corresponding variation in elongation, and I wonder if there is not some other cause to which we could assign the variations in the elongation, perhaps some variation in method of test? After all, grain size is simply a symptom of either chemical or physical pretreatments, and I do not think we have sufficient variation in the treatment of these samples to show variation in any property.

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* Baker & Co., Inc.

E. M. Wise.—I do not quite understand the point. These materials were initially annealed at 1100° C. That will lead to fairly large grain size in pure platinum and somewhat finer ones in the rhodium platinum, and so on. The effect of grain size was most markedly involved in the earlier tests on the effect of annealing at various temperatures on properties.

C. S. Sivil.—Near the beginning of the paper you say: "The elongations of the nearly pure platinums are somewhat erratic, probably because of the large grain size."

E. M. Wise.—I think that is a true statement.

C. S. Sivil.—My experience is that no matter how the grain size varies in pure platinum, the elongation runs between 37.5 and 40 per cent in a 2-in. gauge length.

E. M. Wise.—If the grain size becomes a fair fraction of the elongation, it may cause a rather violent departure from that particular sample from the mean.

H. E. Stauss.—In our work on fine wires, we did not try to measure the elongation but in several we measured the change in diameter a short distance back of the break in order to determine the elongation. We found the elongation of pure platinum—that is, the reduction in cross section some distance back of the break—to be only about half that for the alloys, just contrary to what might be expected.

E. M. Wise.—Recrystallization probably occurred during the test did it not?

H. E. Stauss.—During the test, yes.

E. M. Wise.—As far as variation in reduction of area is concerned, it is so high that it is not very sensitive to anything but rather gross effects, and another difficulty with it, at least in our hands, is that sometimes it is rather hard to measure because the contour makes it a little difficult to see what finally constituted the broken area. Such severe necking occurs that when the shadow of the wire is projected on the screen for measurement it is sometimes difficult to decide just what to measure when the reductions are of the order of 95 per cent or above.

Indium-treated Bearing Metals

By C. F. Smart*

(New York Meeting, February, 1938)

Since their comparatively recent development, the alloys of cadmium with silver and copper or nickel, and of cadmium with nickel alone, have been used somewhat extensively as liners for connecting rod bearings and main bearings of internal-combustion engines. In applications where, owing to high bearing loads and elevated operating temperatures, the life of bearings made from tin-base or lead-base alloys has been undesirably short, cadmium alloys have demonstrated considerable advantage. In applications where, because of deflection of the crankshaft or bearing supports, copper-lead bearing metals have resulted in scored shafts, cadmium alloys have been operated successfully.

The somewhat serious drawback to these alloys in bearing service has been that they, in common with copper-lead and certain lead alloys, are susceptible to corrosion in the presence of lubricants containing organic acids. These acids may be fatty acids (such as oleic acid) derived from animal or vegetable oils that sometimes have been compounded with engine lubricants, or they may be compounds of an acid nature developed by the oxidation of some petroleum oils under operating conditions. The result of such acid attack on bearings is illustrated by the photograph, Fig. 1.

The petroleum oils that are most readily oxidized to a corrosive condition, and the operating conditions under which such oxidation most readily occurs, are now rather well known among the technical organizations of both the petroleum and automotive industries. While means have been developed for inhibiting petroleum oils against such acid formation, the knowledge that this condition may be encountered has been a factor in restricting the wider use of cadmium alloys as engine bearings. It has appeared, therefore, that their value and use would be enhanced if they could be made corrosion-resistant to a degree compatible with the most severe operating requirements.

Investigation, undertaken with this in view, indicated that the addition of fractional percentages of the metal indium to the cadmium bearing

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Manuscript received at the office of the Institute Dec. 1, 1937.

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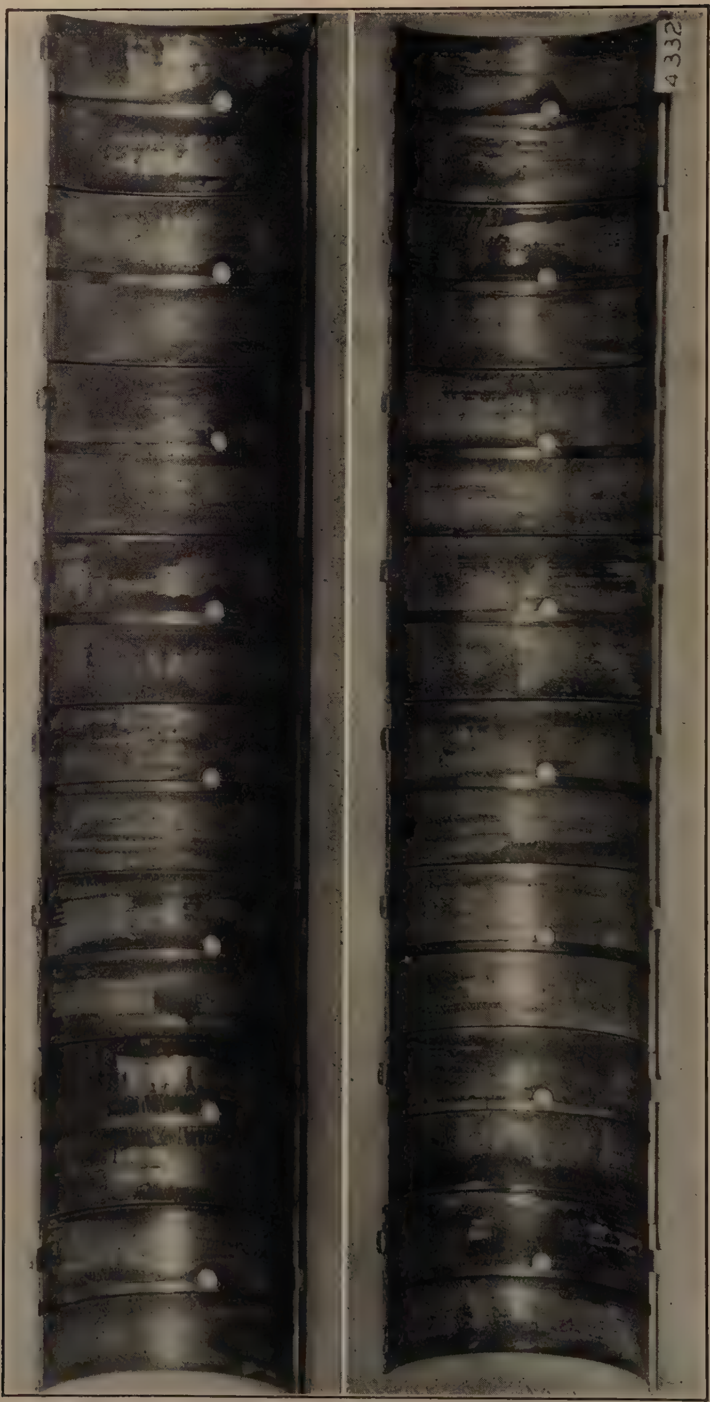

FIG. 1.—BEARINGS CORRODED BY CORROSIVE LUBRICANT.

alloys resulted in excellent corrosion resistance without detriment to their desirable bearing-metal features. This investigation resolved into several stages:

1. A laboratory survey of the effect that various metals might have on the corrosion resistance of cadmium or cadmium alloys.
2. Tests of bearings made from alloys that appeared to offer improvement in this regard.
3. Development of a suitable method of treating bearings with indium.
4. Supplementary tests to check results.

In the laboratory survey the effect of a number of metals alloyed with cadmium was checked by utilizing lubricants of demonstrated corrosive properties for the corroding media, in accordance with the following procedure:

Alloys were made up from weighed components by melting under zinc chloride flux and casting the metal into small flat ingots. From these test pieces approximately 3 by ⅜ by ¼ in. were cut and the surfaces polished smooth. (Samples that were taken from bearings were prepared by flattening a half bearing and cutting into suitable strips.) The cleaned and weighed test pieces were placed in 250-c.c. beakers, along with 135 c.c. of oil and heated in an electric oven held at 340° F. At intervals the specimens were removed, cleaned and weighed, and the extent of corrosion was judged according to weight loss and appearance. The test pieces were long enough to project above the oil surface, and generally any corrosion began at this surface line of contact. Three lubricants were used: (1) new petroleum oil of a brand known to oxidize to an acid condition, (2) preoxidized oil of the same brand, (3) a nonacid-forming petroleum oil to which was added 5 per cent by volume of lard oil.

Results of Beaker Corrosion Tests

Table 1 is a compilation of corrosion data for the alloys of cadmium that were tested in the manner described. The numbering system is the same as that used in a previous paper giving results of certain physical tests on a number of these alloys.[1] Some of the alloys listed in Table 1 were not mentioned previously and for these the physical test data are included in Table 2.

Of the alloys examined, only those with tin, zinc or indium additions appeared to offer improvement in resistance to corrosion. Tin in amounts as low as 0.16 per cent appeared definitely beneficial in this regard, but even with tin as low as this the alloys were extremely brittle. The alloys that contained zinc in amounts equal to or greater than the eutectic composition (17.4 per cent Zn) were somewhat corrosion-resistant as shown by these tests, and had good hardness and toughness characteristics.

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[1] References are at the end of the paper.

TABLE 1.—*Data on Laboratory Corrosion Tests*

Specimens heated at 340° F. for time shown. Corroding media: (1) corrosive type of mineral oil, (2) preoxidized corrosive type mineral oil, (3) mineral oil plus 5 per cent lard oil

No.	Composition, Per Cent	Corrosion Medium	Time, Hr.	Weight Loss, Grams	Remarks
Group I	Cd	3	24		Yellow deposit below oil surface, etched at surface line.
Group II	Cd- Ag				
2-4	2.88	3	24	0.0297	Etched at surface line of oil.
Group IV	Cd- Ag - Cu				
4-3	1.0 1.25	1	144	0.1350	Corroded.
4-15	2.88 0.124	3	24	0.0402	Etched at surface line of oil.
4-17	2.88 0.248	3	24	0.0480	Etched at surface line of oil.
Group V	Cd-Mg				
	0.37–0.39	3	24	0.0180	Blistered.
Group VI	Cd- Cu - Mg				
6-1	0.125 0.10	3	24	0.0235	Blistered, etched.
Group VII	Cd-Ni				
	Sample commercial bearing	3	24	0.0270	Etched.
Group VIII	Cd-Ag- Ni				
8-1	1.0 1.0	3	22	0.0105	Etched at surface line of oil.
8-2	1.5 0.5	3	22	0.0095	Etched at surface line of oil.
		2	22	0.0190	Etched at surface line of oil.
Group IX	Cd-Ag- Cu - Ni				
9-1	2.5 0.25 0.25	3	22½	0.0250	Etched at surface line of oil.
9-2	2.5 0.25 0.50	3	22½	0.0245	Etched at surface line of oil.
Group X	Cd- Zn				
10-1	16.6	3	22	0.0040	Etched below oil surface.
		2	22	0.0280	
10-2	20.0	3	17	0.0890	
		2	22	0.0330	
Group XIII	Cd-Ag- Cu - Zn				
13-1	2.0 0.20 0.25	3	24	0.0060	Slight etch.
13-2	2.5 0.25 0.25	3	21½	0.0115	
13-4	2.5 0.25 0.50	3	70	0.1295	Considerably etched.
13-5	2.5 0.25 1.00	3	66	0.0820	Considerably etched.
13-7	2.5 0.25 5.00	3	24	0.0560	Considerably etched.
13-8	1.5 0.30 12.50	3	22	0.0165	Etched below surface line of oil.
		2	22	0.0445	
13-9	1.5 0.43 13.9	3	22	0.0120	Etched below surface line of oil
13-10	0.6 0.10 21.8	1	240	0.0030	Not etched.
Group XV	Cd- Ag - Sb				
15-1	1.44 0.44	3	20		Etched at surface line of oil.
Group XVI	Cd- Ag - Cu - Sb				
16-1	1.75 0.25 0.25	3	23	0.0420	Etched at surface line of oil.
Group XVIII	Cd-Ag- Cu - Ni - Sb	3			
18-1	2.5 0.25 0.38 0.47	3	24	0.0695	Etched at surface line.
Group XIX	Cd- Sn				
19-1	0.05	3	18½	0.0090	Some etching.
Group XX	Cd- Ag - Cu - Sn				
20-1	1.95 0.25 0.05	3	24	0.0210	Etched.
20-2	2.88 0.25 0.20	3	21	0.0010	No visible corrosion.
20-3	8.00 Tr 0.16	3	20		Stained, but no visible corrosion.
Group XXI	Cd- Cu - Hg				
21-1	0.125 0.42	3	24	0.0360	Etched at surface line.
Group XXII	Cd-Ag- Cu - Hg				
22-1	2.5 0.25 1.60	3	24	0.0200	Etched at surface line.
Group XXIII	Cd- In				
23-1	0.33	3	48	0.0000	No corrosion.
Group XXIV	Cd- Ag - In				
24-1	1.92 0.43	2	42	0.0120	Etched at surface line.
Group XXV	Cd- Ag - Cu - In				
25-1	1.50 0.16 0.11	3	24	0.0440	Badly etched.
25-2	0.96 0.25 0.21	1	186	0.0040	No visible corrosion.
25-3	1.25 0.25 0.25	1	240	0.0030	No visible corrosion.
25-4	0.86 0.21 0.375	1	240		No visible corrosion.
25-5	2.25 0.25 0.39	2	22	0.0050	
		3	75		No visible corrosion.
		1	144		No visible corrosion.
25-6	1.91 0.31 0.42	1	240		No visible corrosion.
Group XXVI	Miscellaneous[a]				

[a] Cadmium alloys treated with appreciable quantities of one or more of the following elements did not show corrosion resistance: Lithium, beryllium, sodium, silicon, calcium, cobalt, selenium, tellurium, cerium or gold.

Attempts to alloy cadmium with the following were unsuccessful: Aluminum, titanium vanadium, chromium, manganese, molybdenum, tungsten.

Table 2.—*Physical Test Data for Alloys of Groups XXIII, XXIV and XXV*

Alloy No.	Brinell as Cast	Cold Bend, Deg.	Hot Bend (400° F.)	Treatment	Brinell Hardness Number after Treatment	Bend Test after Treatment, Deg.
23-1	27–28	10–15	(Brilliant fracture)			
24-1	38	30		Cold-hammered 50 per cent	50	
				Cold-hammered and annealed at 340° F.	31	
25-1	36	90	180			
25-2	36–40	90		20 Hr. at 340° F.	32.6	180
25-3	38	45		18 Hr. at 340° F.	31	90
25-4	38	45		70 Hr. at 340° F.	31	180
25-5	43.6	80	100	18 Hr. at 340° F.	38	Brittle
25-6	45	Brittle		240 Hr. at 340° F.	36	90

The cadmium alloys with indium added in amounts of 0.2 per cent and greater showed definite improvement in corrosion properties.

BEARING TESTS

The alloys containing zinc in the quantity indicated as required for corrosion resistance were considered of doubtful value because of the generally poor frictional properties of zinc. However, bearings were made using as lining metal an alloy containing 1.25 per cent Ag, 0.23 per cent Cu, 20.5 per cent Zn and the balance cadmium. Two sets of these were run in an engine, and in each case failure occurred at low mileage by seizure, resulting in scoring of the crankshaft.

The cadmium-tin alloys, even those containing very low percentages of tin, were very brittle and appeared weak at elevated temperatures Several engine tests were run, however, on bearings containing tin in small amounts. These failed either by corrosion or by disintegration of the bearing metal.

A bearing metal containing 1.25 Ag, 0.25 per cent Cu and 0.25 per cent In was cast into steel shells using cadmium-zinc alloy as a bonding metal. The resultant bond was very weak and bearings machined from these shells failed after only a short run, because of bond failure. Using cadmium-nickel alloy for the bonding metal, the bond obtained was somewhat stronger, and bearings made in this manner were run over 10,000 miles at a speed of 75 miles per hour. A corrosive lubricant was used for this test and, although the A.S.T.M. acid number of the oil reached a value of 5.1, these bearings showed no evidence of corrosion.

INDIUM-PLATED BEARINGS

Because of the relatively weak bond obtained in several attempts at casting the cadmium-silver-copper-indium alloy onto steel backs, bearings made in this manner were considered unsatisfactory. Accordingly, an alternative method of alloying indium to the bearing metal was tried. This consisted of depositing indium on the bearing surface of steel-backed bearings lined with cadmium-silver-copper alloy and then heating these to obtain alloying and diffusion of the indium into the bearing metal.

The bearings to be plated were in the finished-machined state. They were electrocleaned on the cathode of an alkaline cleaning bath, rinsed with water, and plated in an indium cyanide bath as developed by Gray and reported by Murray.[2] The solution was made up to contain 4 oz. of indium, 2 oz. of dextrose sugar and 12 oz. of sodium cyanide per gallon. The backs of the bearings were protected against plating by a band of thin rubber tubing. The tension of this band also served to maintain good contact between the point of the cathode hook and the bearing-metal surface. Carbon anodes were used and the bath was operated at room temperature. Good deposits of indium were obtained at current densities ranging from 25 to 100 amperes per square foot. The indium plate was very soft, and lightly rubbing with a cloth served to buff the surface smooth and bright. When heated a short time at temperatures of 340° F. or higher the bright surface took on a frosted appearance and could not then be so easily buffed, thus indicating that the indium had diffused into the bearing metal.

Bearings lined with an alloy containing 2.25 per cent Ag, 0.25 per cent Cu and balance cadmium, which were plated with indium and heated, were investigated (1) to determine the amount of indium plate necessary for corrosion resistance and (2) to check the effect of the plating and diffusion treatment on such properties as bond strength and the strength and toughness of the treated metal at ordinary and elevated temperatures. The results of these tests indicated as follows:

1. That indium in amount calculated to be 0.20 per cent of the bearing metal definitely improved corrosion resistance and that 0.4 to 0.5 per cent In was sufficient to withstand corrosion under most severe conditions.
2. That diffusion was rapid at temperatures of 340° F. and higher, the soft indium layer appeared to be alloyed after 30 min. at 340° F. and diffusion through 0.010 to 0.015 in. of bearing metal appeared to be accomplished in 2 hours.
3. That heat-treatment at 450° F. weakened the bond strength on some bearings bonded with cadmium-zinc alloy, but did not weaken the bond strength on bearings bonded with cadmium-nickel alloy; heat-treatment at 500° F. lowered the bond strength of both types.

4. That heat-treatment at 340° F. did not weaken the bond strength of unplated bearings bonded with cadmium-zinc, but 2 hr. heating at this temperature seriously weakened the bond on similar bearings that had been plated with indium. This was also found to be true for bearings of this type electroplated with tin, but was not evident when cadmium plate was substituted for indium or tin, indicating that the latter metals have a weakening effect when they penetrate to the cadmium-zinc bond layer.

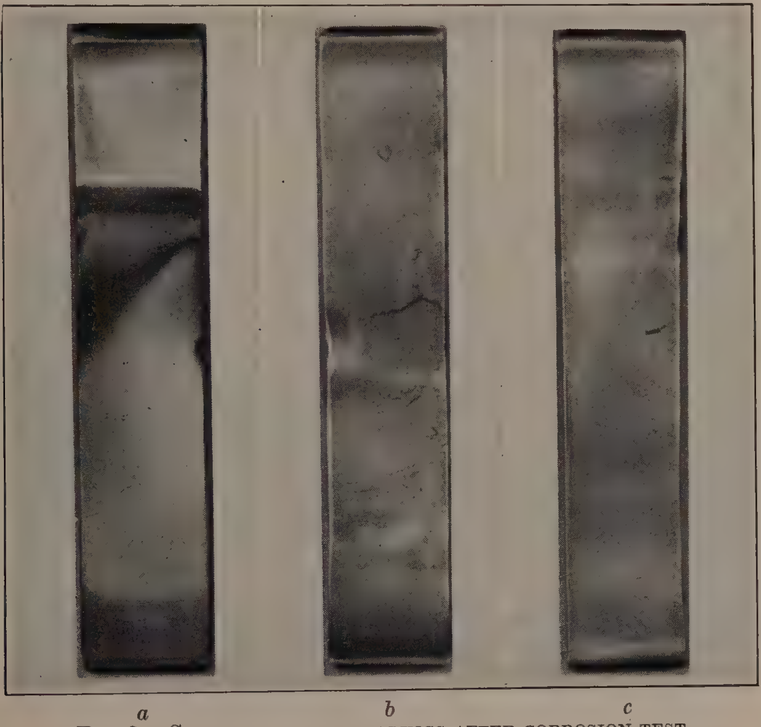

FIG. 2.—SPECIMENS FROM BEARINGS AFTER CORROSION TEST.

a. Cadmium-silver-copper bearing, No. 0. Diffused 96 hr. at 340° F. in corrosive oil. Loss, 0.1370 grams. Badly corroded.

b. No. 97, bearing plated with 0.0170 grams indium. Diffused 18 hr. at 340° F.; 144 hr. at 340° F. in corrosive oil. Loss, 0.0290 grams. Visibly corroded.

c. No. 75, bearing plated with 0.0290 grams indium. Diffused 2 hr. at 340° F.; 216 hr. at 340° F. in corrosive oil. Loss, 0.0120 grams. No visible corrosion.

5. That heat-treatment at 340° F. of bearings bonded with cadmium-nickel and plated with indium did not weaken the bond strength even when held at this temperature for 60 hours.

6. That indium in amounts calculated to give up to 0.5 per cent of the bearing metal did not appear to embrittle the cadmium-silver-copper alloy. Appreciably greater amounts of indium did result in embrittlement, increasing as the amount of indium was increased.

The relative corrosion resistance of cadmium-silver-copper bearings plated with indium and diffusion heat-treated was determined by laboratory beaker corrosion tests, using preoxidized corrosive lubricant, on the following:

Sample 0, untreated bearing.

Sample 97, bearing plated with indium in amount calculated to be 0.22 per cent by weight of bearing metal, heated 18 hr. at 340° F.

Sample 75, bearing plated with indium in amount calculated to be 0.38 per cent by weight of bearing metal, heated 2 hr. at 340° F. Results for samples cut from these are listed in Table 3.

TABLE 3.—*Beaker Corrosion Tests on Cadmium-silver-copper Bearings*
WEIGHT LOSS, GRAMS

Sample	24 Hr.	48 Hr.	96 Hr.	144 Hr.	216 Hr.
0	0.0380		0.1370		
97		0.0050		0.0290	
75		0.0060			0.0120

Fig. 2 is a photograph of the samples listed in Table 3, showing the condition of the bearing surface at the conclusion of the test.

As a check on these results, indium-plated and diffusion-treated bearings of this type were tested for corrosion by General Motors Research Laboratories in the Underwood corrosion-test apparatus. The bearing-metal surface was exposed for 5 hr. to a fine spray of oxidized lubricant at a temperature of 325° F. Results from tests in which oil with 1 per cent oleic acid added was used are shown in Table 4.

TABLE 4.—*Corrosion Tests on Cadmium-silver-copper Bearings*

Sample	Weight of Indium, Grams	Percentage of Indium (Calculated)	Diffusion Treatment, Hr. at 340° F.	Weight Loss, Grams	Acid No. Oil (A.S.T.M.)
Untreated....				0.87	8.73
32	0.0180	0.24	1	Nil	7.7
33	0.0200	0.26	1	Nil	7.7
37	0.0070	0.09	1	0.17	10.9
38	0.0060	0.08	1	0.31	13.6
40	0.0130	0.17	1	0.08	13.6
196	0.0400	0.53	18	0.03	17.6
197	0.0370	0.49	18	0.07	17.6
206	0.0250	0.33	20	0.02	11.8
207	0.0340	0.45	20	0.02	11.8

The bearing-metal surface of the bearing halves used in the tests described was calculated to be 4.1 sq. inches.

Cadmium-nickel alloy bearings (containing approximately 1.25 per cent nickel) were tested in a similar manner. Typical results on bearing halves with a calculated bearing area of 7.35 sq. in. are listed in Table 5.

TABLE 5.—*Corrosion Tests on Cd-Ni Bearings*

Sample	Weight of Indium, Grams	Percentage of Indium (Calculated)	Diffusion Treatment, Hr. at 340° F.	Weight Loss, Grams	Acid No. Oil (A.S.T.M.)
205	not treated			1.19	9.7
208	0.160	0.55	20	0.00	8.6

Corrosion-fatigue tests were run on indium-treated cadmium-silver-copper bearings at the General Motors Research Laboratories. The equipment used consisted essentially of two engine connecting rods mounted at 90° to one another and held stationary, and an eccentric-weighted steel shaft rotating in the large end bearings. The shaft was rotated at 4500 r.p.m. and the calculated bearing load was 1400 lb. per sq. in. of projected bearing area. SAE-30 oil containing 1 per cent added oleic acid was heated and circulated to the bearings, which were maintained at 345° to 350° F. Fig. 3 is a photograph of this equipment. The data from these tests are tabulated in Table 6. At the end of 100 hr., representing approximately 8500 miles at full load wide-open throttle, with bearing temperature held well above those encountered in service, and in the presence of a corrosive lubricant, the bearings represented by Nos. 147, 173, 168 and 169 still showed remarkably good condition. Fig. 4 is a photograph illustrating the condition of these bearings after this test. For comparison, bearings of the same design but lined with tin-base babbitt ran up to a maximum of 50 hr., failure being due to fatigue of the bearing metal.

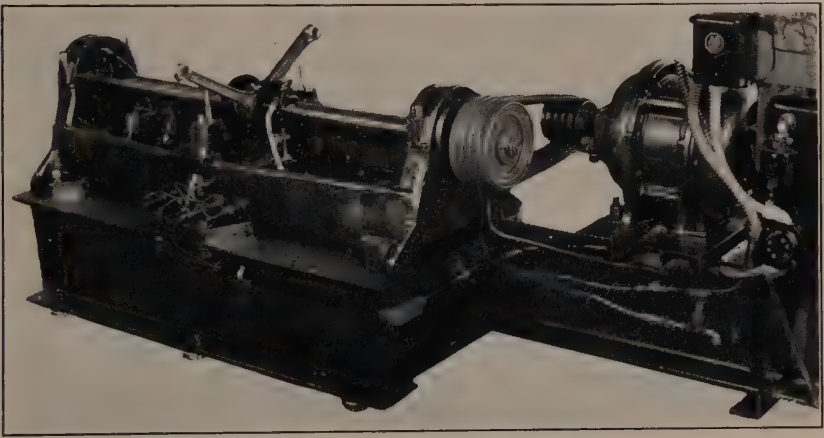

FIG. 3.—FATIGUE-TESTING EQUIPMENT.

Comparative corrosion tests were made on untreated cadmium-silver-copper, copper-lead, and indium-treated cadmium-silver-copper bearings by one of the major oil companies. The test apparatus, developed by the oil company, is shown in Fig. 5. The bearings were assembled in connecting rods and a rotating shaft served to remove any protective film that might be formed on the bearing surface. The bearings were held at 340° F., oil at 30-lb. pressure was circulated to them and air at 90 cu. ft. per hour was passed through the oil chamber. Corrosion results after 22 hr. were as given in Table 7.

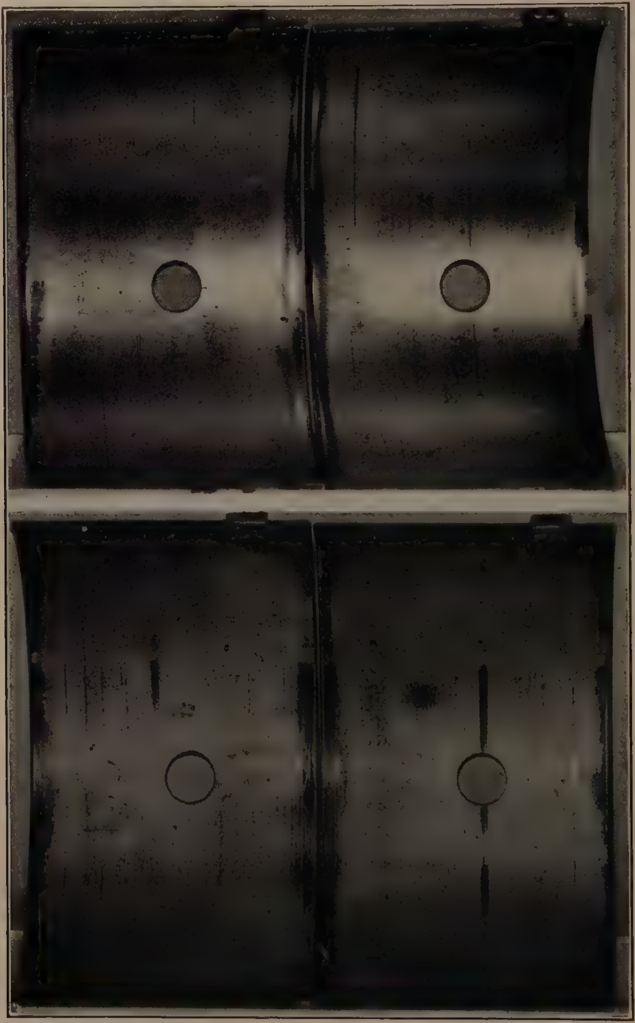

Fig. 4.—Bearings 168, 169, 147 and 173, indium-plated and diffused, after 100 hours corrosion-fatigue test.

At the conclusion of this test the untreated cadmium-alloy bearing was severely corroded while the indium-treated bearing was smooth and bright with no appearance of etching.

Copper-lead bearings have also been subject to attack by corrosive oils in service and tests have indicated that this type of bearing is also

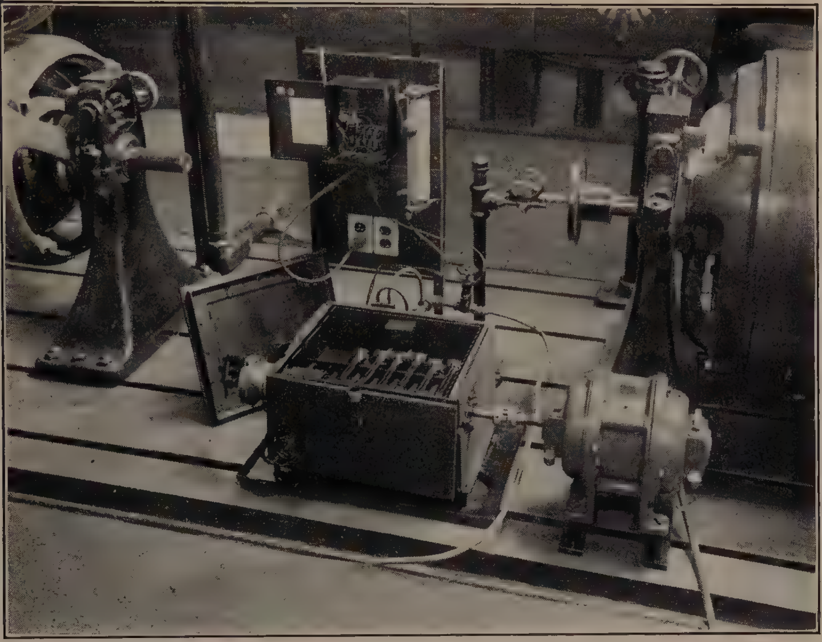

FIG. 5.—CORROSION-TESTING APPARATUS (SIBLEY).

TABLE 6.—*Corrosion-fatigue Tests on Cadmium-silver-copper Bearings*
SAE-30 Oil plus 1 Per Cent Oleic Acid

Sample No.	Wt. Indium, Grams	Indium, Per Cent (Calculated)	Diffusion Treatment, Hr. at 340° F.	Duration of Test, Hr. at 345°–350° F.	Wt. Loss, Grams	Thickness Loss, In.
Untreated bearing...				$6\frac{1}{4}$	Bearing metal almost completely gone	
142	0.0180	0.24	20	50	0.20	0.0004
				$77\frac{5}{12}$	5.43	0.012
143	0.0165	0.22	20	50	0.17	0.0004
				$77\frac{5}{12}$	5.18	0.018
144	0.036	0.48	20	50	0.02	0.000
				$77\frac{5}{12}$	0.08	0.0005
145	0.037	0.49	20	50	0.07	0.0000
				$77\frac{5}{12}$	0.22	0.0005
166	0.037	0.49	20	100	0.01	0.000
167	0.037	0.49	20	100	0.10	0.000
168	0.037	0.49	20	100	0.02	0.000
169	0.037	0.49	20	100	0.00	0.000
147	0.065	0.69	20	50	0.02	None
				100	0.02	None
173	0.065	0.69	20	50	0.07	None
				100	0.07	0.0001

TABLE 7.—*Comparative Corrosion Tests on Copper-lead, Cadmium-silver-copper and Indium-treated Cadmium-silver-copper Bearings*

Sample	Loss per Half Bearing, Grams	Loss per Sq. In. Bearing Surface, Grams
Cd-Ag-Cu (untreated)	3.2232	0.821
Copper-lead	0.7536	0.256
Cd-Ag-Cu (indium-treated)[a]	0.0030	0.001

[a] Plated with 0.0350 grams indium (0.46 per cent In calculated) diffused 2 hr. at 340° F.

protected by treatment with plated and diffused indium. Results from the Underwood corrosion test on copper-lead bearings so treated are given in Table 8.

TABLE 8.—*Underwood Corrosion Test on Copper-lead Bearings*[a] *Treated with Indium*

Sample	Wt. of Indium, Grams	Diffusion Treatment, Hr. at 340° F.	Wt. Loss, Grams	Acid No. Oil (A.S.T.M.)
209	0.0570	20	0.08	17.6
210	0.0580	20	0.06	17.6
Untreated			0.37	8.7

[a] Bearing-surface area, 4.1 sq. in.

ENGINE TESTS ON PLATED BEARINGS

In one engine test connecting rod bearings lined with cadmium-silver-copper alloy, treated with approximately 0.20 per cent In, were run for over 5000 miles at high speed. At the conclusion of the test these bearings showed only slight evidence of etching, whereas untreated bearings run in one of the connecting rods were replaced three times because of their badly corroded condition. The acid number of the oil used reached a value of 3.3.

In another engine the fatigue life of babbitt-lined bearings ranged up to a maximum of about 60 hr. under the severe conditions used for testing (4250 r.p.m., full throttle, with oil temperature 250° to 260° F. at the bearings). Cadmium-silver-copper bearings treated with 0.4 to 0.5 per cent In run under these test conditions, and in the presence of oil containing 0.5 per cent of oleic acid, were in excellent condition after 120 hr., showing no evidence of corrosion and very slight indication of fatigue cracks.

Such tests on bearings, in engines run at high speed and with corrosive oils, verify the information obtained from laboratory tests—namely, that the indium treatment as described prevented corrosion of the cadmium-alloy bearings without impairing the fatigue resistance or other bearing-metal properties.

REFERENCES

1. C. F. Smart: Cadmium-Silver-Copper Alloys for Engine Bearings. *Trans.* Amer. Soc. Metals, **25**, No. 2, 571.
2. William S. Murray: Production and Deposition of Indium. *Ind. and Eng. Chem.*, **2**, No. 20, 300.

DISCUSSION

(*R. M. Burns presiding*)

H. J. HUGHES,* New York, N. Y. (written discussion).—Mr. Smart is to be congratulated on a contribution that will not only permit an extended use of improved bearing materials but will unshackle the chemists in the oil industry, so that they may continue their development of improved refining processes and useful addition agents.

When the corrosion of cadmium and lead-bronze bearings was first uncovered, addition agents were singled out as Bearing Enemy No. 1 and there was a rush on the part of manufacturers employing these new bearings to warn that nothing but pure petroleum oils were necessary or desirable for their engines. However, it was not long before the discovery was made that solvent refined oils were just as corrosive as oils containing addition agents, and before the investigation was completed even some of the old reliable Pennsylvania oils joined the bearing enemy list.

With regard to the other parts of the engine, the results of improvements in lubricating oil were showing to good advantage. Solvent refining produced lubricants with better viscosity index and lower carbon content, and the addition of metallic soaps reduced gum and sludge formation by eliminating the catalytic effect of the ferrous metals in the oxidation process. The question that was now before the oil industry was how much of this improved lubrication of other parts should be sacrificed in order to prevent corrosion of the bearings. A great deal of research work was devoted to the development of substances that could be added to the oil to prevent or inhibit the corrosion of the bearings. A number of corrosion inhibitors, as they were termed, were found, and some were, and still are, used commercially, as referred to in Mr. Smart's paper. Our work with these corrosion inhibitors has indicated that many of them increase the tendency of the oil to form gums and sludges when oxidized at high temperatures in the presence of an active catalyst such as iron, and the addition of such corrosion inhibitors to the oil serves to defeat, to some extent, the effect of metallic soaps, which are added to reduce sludge and gum formation.

During the past year both the engine builders and the oil industry have given more attention to the use of addition agents to compensate for the natural deficiencies in petroleum lubricating oil. Evans and Kelman have shown the catalytic action of iron and how it may be overcome by the addition of metallic soaps to the lubricant. Rosen has shown the value of addition agents in Diesel engine lubricants, and experience with high-output aircraft engines has indicated that petroleum oils lack the necessary qualities to prevent ring sticking unless they are treated with certain additives. It might also be observed that the engines that can use cadmium or lead bronze bearings to the best advantage are those most in need of lubrication superior to that provided by pure petroleum oils. From this it is obvious that the tendencies of cadmium and lead bronze bearings to corrode have been a limiting factor in development of lubricating oil.

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* C. C. Wakefield & Co., Ltd.

Mr. Smart has treated a few bearings for us, and we have experimented with these using commercial lubricants, some of which have been treated with metallic soaps. In these tests we have used an apparatus developed by Mr. Sparrow, of the Studebaker Corporation. We prefer it because it is simple, easy to clean, and because the bearing surfaces are continually wiped by metallic rollers, also the temperatures and procedure can easily be varied to suit the type of oil being tested. Table 9 shows our results on indium-treated bearings as compared to standard bearings of the same make. The lead bronze bearings were each plated with 0.0230 to 0.0280 gram of indium. The cadmium-silver bearings on oil A were plated with 0.0250 to 0.0280 gram of indium, and for oil B with 0.0180 to 0.0220 gram of indium, the time for diffusion being 3 hr. in each instance. Our work on the cadmium bearings is not yet completed, but the indications from those we have tested so far are that the cadmium bearings will be as immune to corrosion as the lead bronze bearings are.

The results of our tests confirm those reported in Mr. Smart's paper, and seem to indicate that with the discovery of indium treatment the way has been opened for engine builders to take full advantage of cadmium and lead bronze bearings without retarding the development of the lubricating-oil addition agents which have been so successful in solving other engine problems.

TABLE 9.—*Comparison of Indium-treated and Standard Bearings*

Oil	Specific Gravity at 60° F.	Viscosity, Sec.	Type	Addition Agents	Corrosion Loss, Grams				Remarks
					Standard Lead Bronze	Indium-treated Lead Bronze	Standard Cadmium-silver	Indium-treated Cadmium-silver	
A	0.880	At 100° F. 345	Ordinary refined	Metallic oleates	220° F. 0.1086	220° F. 0.0072	270° F. 1.0636	270° F. 0.0030	
B	0.892	At 100° F. 570	Ordinary refined	Metallic oleates	220° F. 0.2116	220° F. 0.0051 270° F. 0.0861	270° F. 1.7696	270° F. 0.0013	
C	0.906	At 210° F. 78	Ordinary refined	Fatty oil	220° F. 0.0997	270° F. 0.0166			
D	0.893	At 100° F. 300	Solvent refined	None	220° F. 0.3427	220° F. 0.0250			This oil preoxidized at 350° F. for 24 hr. in presence of active catalysts

E. E. SCHUMACHER,* New York, N. Y.—What is the present availability and price, say per pound, of indium? How would the present price of the metal be affected by a great increase in demand for it?

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* Metallurgist, Bell Telephone Laboratories.

A. J. Phillips,* Barber, N. J.—Assuming that indium-treated bearings are completely resistant to corrosion by these special oils, are there no other parts in internal-combustion engines that will be corroded and thus prevent the use of such oils?

A. M. Setapen,† Washington, D. C.—In this study, did the author do anything with the friction characteristics of this indium-treated bearing?

N. B. Pilling,‡ Bayonne, N. J.—A few years ago the Institute produced a volume on the uses of nonferrous metals in which the word "indium" does not even occur in the index. In one of the standard chemical reference books is found this statement: "Indium is one of the rarest of the elements, occurring in minute quantities widely distributed in nature." A few comparative figures are given on the relative abundance of some of the rarer metals in comparison with indium. These percentages are so microscopically small that I will not try to quote them, but the abundance of gold and platinum is about 100 times that of indium, and this metal is said to be only $\frac{1}{10}$ as scarce as radium. Is there indium enough in one spot to support so interesting and important an application as this?

If Mr. Smart will share his secret with us, I should like to know how he so quickly came to such a productive line of study on these bearings. I think indium is something that would not occur to a good many of us.

T. A. Wright,§‖ New York, N. Y.—If I understand correctly, rhenium apparently affects the corrosion of the zinc shell of the dry-cell battery, and yet one worker never found that rare element in all his studies here and abroad in a greater amount than 1×10^{-4}. Out of some 56 examinations of pyrolusite, in 18 he found rhenium. The 18 represented as many subnormal batches of dry cells, which had a faulty shelf life. That is all I know about that story.

As to the possible effects of these cryptotrophic elements as to occurrence and also amounts, we have found that indium is a common constituent of all of the refined tins from abroad that we have examined, and I suggest to Dr. Derge that he keep that in mind and perhaps repeat some of his work on reference standards from some of the tin that is recovered from tin tetrachloride wastes, which contains, so far as I know, no indium, no bismuth, and no silver, and may be of a somewhat higher purity than some Chempur may be. Maybe we will find out a little bit more about this at the next A.S.T.M. meeting, but there is a question of a minute element which does occur regularly and the effect of which is not known. It might have an effect on the film and might even have an effect, if the story about rhenium is true on the corrosion resistance of tin.

C. F. Smart.—The question was asked regarding the behavior of indium-treated bearings with certain of the compounded lubricants. I think this refers to lubricants developed particularly for Diesel engine operation to overcome ring sticking. We have run indium-treated bearings successfully in Diesel engines with these oils, and have found that they do withstand the compounded oils very well.

In some of the bearings we treated for Mr. Hughes, the indium content was purposely held to the low side of what we thought would be successful, from an economic viewpoint.

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* Superintendent of Research, Central Research Laboratories, American Smelting and Refining Co.

† National Bureau of Standards.

‡ Manager, Research Laboratory, International Nickel Co.

§ Secretary and Technical Director, Lucius Pitkin Inc.

‖ This discussion refers also to the paper by G. Derge, page 391, this volume.

Mr. Schumacher brings up a question that has been raised a number of times. I would answer by saying that we are assured by at least one source that we have worked with that indium can be made available to any extent that the bearing industry may be interested in. From the practical point of view, with indium at its present cost, the cost per bearing of the ordinary engine bearing would probably be somewhere around three or four cents, which for uses such as for Diesel and airplane engines would not be out of commercial range. At from fifty cents to a dollar an engine, depending on the size of the bearings, I think it may be considered commercial.

Dr. Phillips asked a question about corrosion of other engine parts. We know that pistons have been treated with tin (both iron pistons and aluminum pistons) to prolong their life. Rod bushings treated with indium are showing excellent resistance to acid-containing lubricants.

As regards the frictional characteristics of the indium-treated bearings, we have no definite frictional measurements, but we can say that in all our tests on fatigue and corrosion we have not found any scored or worn shafts that would indicate undesirable frictional characteristics. In fact, with some of the copper-lead bearings that have been treated, we think we have considerably improved the frictional characteristics. The cadmium alloys have very good frictional characteristics, anyway, and although there has been no improvement, I doubt if there has been any detriment, certainly not that we could notice.

In reply to Dr. Pilling's question as to how we so quickly arrived at the indium treatment, I would not say that we did do so quickly. We have been working on it for several years, and tried out a great many elements. In fact, we went nearly through the periodic table.

Properties of Alloys of Cadmium and Mercury with Small Percentages of Nickel

By Telfer E. Norman,* Student Associate, and Owen W. Ellis,† Member A.I.M.E.

(New York Meeting, February, 1937)

The use of cadmium as a base for bearing metals is one of the most interesting recent developments in this field. It has caused a strong demand for cadmium and a marked rise in its price. It appeared to the authors, therefore, that the situation might be relieved for users if acceptable substitutes could be developed.

A preliminary investigation has revealed that to some extent mercury may be substituted for cadmium. Whether its use is justified cannot be stated at this time. Most of the authors' work has indicated that the addition of mercury to alloys of cadmium and nickel detracts from their desirable physical properties; but this work has not been extended to cover service tests, which might reveal that the addition of low percentages of mercury to the cadmium-base alloys would improve their performance. The results of tests made by the authors are therefore briefly summarized for this paper. Table 1 gives the proportions of the metals used in preparing the alloys. After preparation of these alloys, their composition was checked by chemical analysis. Particular care was taken to ensure that the nickel content did not vary appreciably from 1 per cent.

Table 1.—*Proportions of Metals Used in Preparing Alloys*

Cadmium, Per Cent	Mercury, Per Cent	Nickel, Per Cent
99	0	1
95	5	1
90	10	1
85	15	1
80	20	1
75	25	1
70	30	1
65	35	1
60	40	1

Manuscript received at the office of the Institute April 17, 1937.

* Research Metallurgist, Ontario Research Foundation, Toronto, Canada.

† Director of Metallurgical Research, Ontario Research Foundation, Toronto, Canada.

Melts of the alloys were made under hydrogen, zinc chloride, and molten sodium hydroxide. The most satisfactory cover was found to be sodium hydroxide. From these melts were poured chill castings in the form of cylinders ½ in. in diameter, from which specimens were cut for the study of their microstructure, compressive strength, and tensile strength. Chill castings in the form of flat bars were also prepared; these were planed down to ¼ by ¾-in. cross section, and were used thus for cold-bend tests. Brinell hardness determinations and cold-rolling tests were also carried out on chill-cast specimens of the alloys.

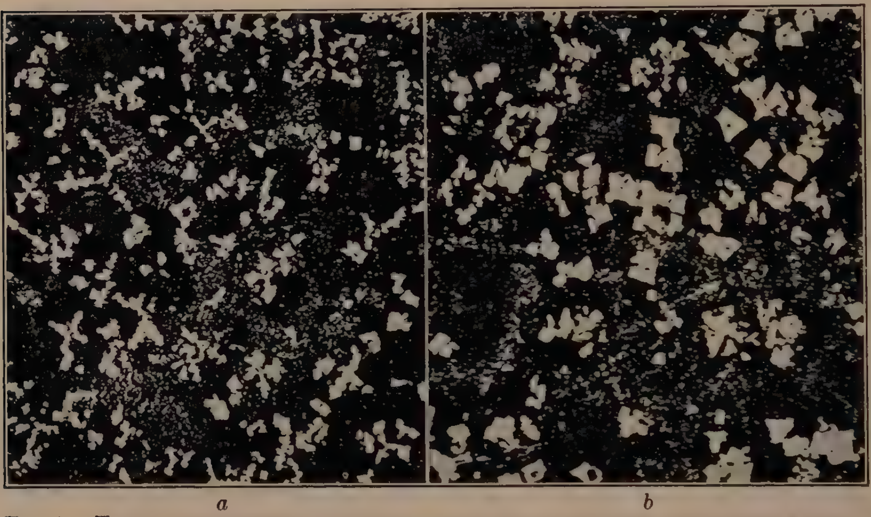

FIG. 1.—TYPICAL MICROSTRUCTURES OF ALLOYS IN CADMIUM-MERCURY-NICKEL SERIES. × 200.
a, 20 per cent Hg, 1 per cent Ni; *b*, 35 per cent Hg, 1 per cent Ni.

Fig. 1 shows typical microstructures of alloys in this series. No definite change in microstructure could be noticed as the mercury content increased from zero to 40 per cent.

The curves in Fig. 2 summarize the results of physical tests on the alloys, showing that by the addition of mercury the compressive and tensile strengths were proportionately lowered. In the compressive tests the test pieces were 0.437 in. in diameter and 0.437 in. high. Stresses were applied from zero to maximum in increments of 500 lb. per square inch. Each load was applied for one minute, the height of the sample being measured after its application. The test was concluded when the specimen had been reduced by 10 per cent of its original height. The stress required to produce this deformation was arbitrarily defined as the compressive strength.

The curve in Fig. 2 for percentage elongation was determined from the tensile tests by the usual method. Tensile-test pieces were one-half the standard size—i.e., they were ¼ in. in diameter and had a 1-in. gauge length. The change in ductility, as indicated by the curve for percentage elongation, agrees very well with the values for this property as indicated by the results of cold-bending and cold-rolling. It is the authors' opinion that this is due to formation of an intermetallic compound, probably Cd_3Hg.

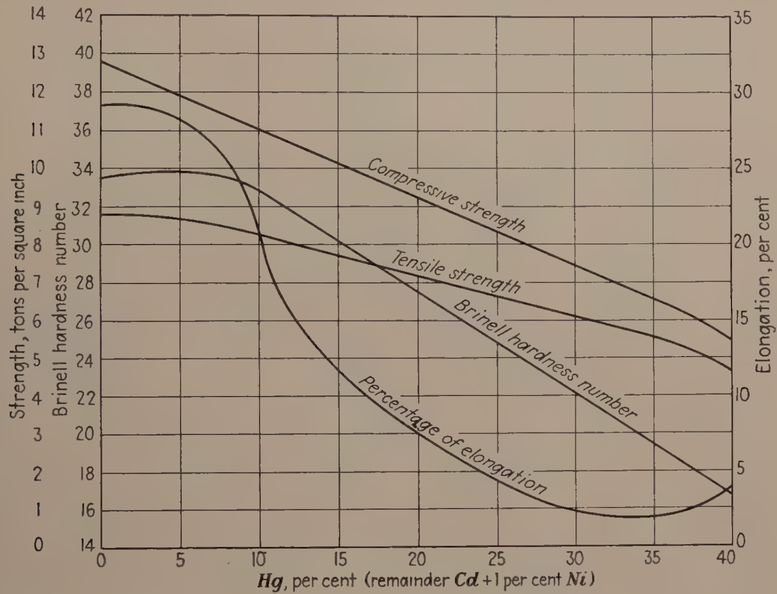

FIG. 2.—SUMMARY OF PHYSICAL TESTS ON CADNIUM-MERCURY-NICKEL ALLOYS.

While mechanical tests have shown these alloys to be inferior to the plain cadmium-nickel alloys, it should be noted that most of them were superior to the commoner tin-base bearing metals, so that from this angle the authors' results can scarcely be considered negative.

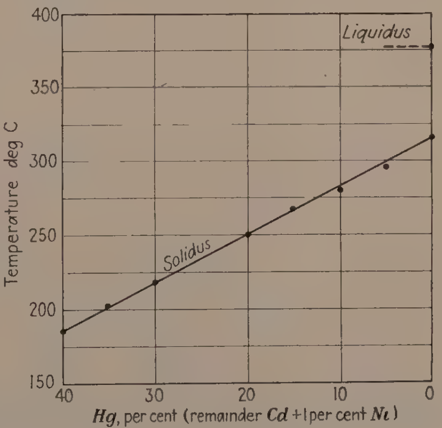

FIG. 3.—SOLIDUS LINE FOR CADMIUM-MERCURY-NICKEL ALLOYS.

Since it appeared that the alloys might lose mercury by evaporation when heated to the working temperatures of bearings, an attempt was made to measure the vapor pressure of mercury at the surface of the hot alloys. A known volume of hydrogen was passed slowly through a Pyrex tube containing filings of the alloy, the tube being immersed in a bath at constant temperature. The mercury evaporated to the hydrogen was allowed to condense at a suitable point where it was collected by chemical means and weighed as HgS. From the data thus obtained the vapor pressure of mercury at the surface of the alloys was calculated, the resulting values for this pressure being from one-half to one-tenth of that demanded by Raoult's Law of Partial Pressures. The presence of oxide films on the surface of the filings was found to lower definitely the vapor pressure of mercury at the surface of the alloys. Since hydrogen would not have reduced cadmium oxide at the temperature of the tests, probably the presence of oxide films caused the very low vapor pressure of mercury in these alloys.

Strips of the alloys were then immersed in hot oil, and the rate of evaporation of mercury from them was determined. In this test practically no mercury was found to evaporate from the alloys at any temperature below their melting points. They did, however, lose weight slowly by chemical attack when the temperature of the oil was raised to 150° C. or over. In general, the high-mercury alloys lost more weight than did the low-mercury alloys.

An attempt was also made to determine the solidi and liquidi of the alloys. Cooling curves were obtained, which, however, did not indicate clearly the critical points. The variation in resistance with change in temperature was therefore determined for the alloys, with the result that the solidi were well indicated. The liquidi, however, were very difficult to determine, and the results obtained were uncertain. Fig. 3 therefore shows only the solidus line for the alloys of the series.

Effect of Tellurium on Mechanical Properties of Certain Copper-base Alloys

By H. L. Burghoff,* Member A.I.M.E., and D. E. Lawson†

(Atlantic City Meeting, October, 1937)

The presence of tellurium in copper and, by inference, in copper alloys, has been considered seriously detrimental and has been avoided. In particular, very small amounts of tellurium have been found to produce red-shortness, although the effects on cold-working and ordinary physical and mechanical properties have not been known so definitely. References in the literature are few, but as long ago as 1881, Egleston[1] reported that 0.083 per cent tellurium in fire-refined copper rendered the copper red-short and therefore worthless for hot-rolling. In hot-rolling copper cakes containing this amount of tellurium, he found that fine cracks appeared in the cakes on the first pass through the rolls, the cracks opening further in successive passes. When cold, the metal was said to be tough and malleable.

A few years ago, during the course of an investigation in our laboratory on copper-base alloys, it was found that tellurium-bearing alloys could be machined much more freely than similar alloys not containing tellurium. The study was pursued further in this direction, and considerable data were obtained, which indicated that certain tellurium-bearing alloys might have properties of commercial interest. The work eventually led to patent protection,[2] a wide range of tellurium-bearing copper-base alloys being covered.

This article presents results obtained on the effect of tellurium on the mechanical properties of three copper-base alloys: commercial bronze (90 Cu, 10 Zn), 1.5 per cent tin bronze (98.5 Cu, 1.5 Sn), and silicon bronze (96 Cu, 3Si, 1 Zn).

Several alloys were cast in each series, with tellurium content ranging from 0 up to about 1 per cent. The alloys were melted under charcoal in a clay-graphite crucible, using a high-frequency induction furnace, and were cast without undue difficulty in rod form, 1⅝ in. in diameter. Charges for the zinc and tin series were made up from the following materials: cathode copper, electrolytic zinc, tin, and tellurium in slab

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Manuscript received at the office of the Institute July 26, 1937.

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[1] References are at the end of the paper.

form. Alloys for the silicon series were made by melting scrap copper-silicon-zinc alloy and adding tellurium, the bars obtained by this procedure being sounder than those made directly from copper, zinc, silicon-copper and tellurium.

The bars were drawn according to regular mill procedure, no difficulty being encountered except with the commercial bronze alloy containing 0.99 per cent Te, which was rather brittle, breaking several times in process. The bars were finished for test on ½-in. diameter in the following tempers, or in as many of these tempers as the material available for each alloy permitted: (1) as annealed, (2) as drawn from 0.530 in. (11 per cent reduction of area), (3) as drawn from 0.562 in. (21 per cent reduction of area), and (4) as drawn from 0.625 in. (36 per cent reduction of area).

Ordinary Rockwell hardness and tensile tests were made on the material, as well as bend, impact and machinability tests. Bends were made around a pin of ½-in. diameter and through a maximum angle of 135°, observation being made of the angle at which fracture occurred in the rare cases where the rods did not successfully withstand bending through 135°.

For impact tests, a modified Izod type of test was employed, specimens being taken from the full-size round rod and having a 45° V-notch of 0.25-mm. bottom radius, 0.125 in. deep, machined at a distance of 1.10 in. from the struck end. Round specimens of this kind have been extensively used by us with satisfactory results in investigations of copper alloys, having been adopted largely as a matter of convenience. Rod materials have usually been tested, which inherently lend themselves to drawing to any desired size. The only machining necessary to prepare such an impact specimen, therefore, is to square the end and mill the V-notch, which is done in one operation. Thus the machining required to produce the more common specimen of square cross-section is avoided. Moreover, when concerned with an alloy that is too hard to be drawn to the desired size, it is a relatively simple matter to turn the piece down to the proper diameter.

In making the machinability tests, a power-driven hacksaw was used, the number of strokes necessary to sever the test rods being compared with the strokes required to sever a free-cutting leaded brass rod of the same diameter and of the following composition: 60.68 per cent Cu, 3.34 per cent Pb, 0.02 per cent Fe, 35.96 per cent Zn (by difference). The relative machinability values were obtained in a simple manner, being based on the assumption that the machinability of the leaded brass was 100 per cent and on the consideration that machinability of the various alloys varied inversely as the number of strokes required to cut through them. Thus the machinability of a particular material is the ratio, expressed in per cent, of the number of strokes for the leaded brass to the number of strokes for the material under test.

It is realized, of course, that this simple test cannot give a complete idea of machinability, nor even check the results of other laboratory tests, such as drilling, turning, or calculations of energy required to remove unit volumes of metal as chips. However, the test results reported here are reproducible and indicate difference in machinability among alloys of the same type. In the final analysis, results of actual commercial production, as indicated by tool life, feasible cutting speeds, surface finish, etc., are necessary. Even in this case comparisons are not absolutely accurate, as personal opinion is always a factor.

TABLE 1.—*Properties of Tellurium-bearing Commercial Bronze Rods, ½-inch Diameter*

Alloy No.	Temper as Drawn from	Rockwell Hardness		Tensile Strength, Lb. per Sq. In.	Yield Strength (½ Per Cent Elong.), Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Contraction of Area, Per Cent	Relative Machinability, Per Cent	Izod Impact, Ft-lb.	Bends	
		F	B							90°	135°
1. 90.10 Cu, 9.90 Zn (by diff.).	Annealed	53		37,500	11,500	54	85	28	73[a]	OK.	OK.
	0.530″	82	39	41,500	34,500	38	85	28	92[a]	OK.	OK.
	0.562″	91	57	47,500	43,500	26	81	27	107[a]	OK.	OK.
	0.625″	91	64	52,000	47,500	23	83	27	102[a]	OK.	OK.
2. 89.94 Cu, 0.10 Te, 9.96 Zn (by diff.).	Annealed	56		38,000	13,500	52	72	31	74[a]	OK.	OK.
	0.530″	83	40	42,500	35,500	35	71	37	82[b]	OK.	OK.
	0.562″	92	58	48,500	44,000	23	68	38	88[b]	OK.	OK.
	0.625″	93	64	52,500	47,500	19	66	39	70[b]	OK.	OK.
3. 89.97 Cu, 0.25 Te, 9.78 Zn (by diff.).	Annealed	58		39,000	12,500	46	62	43	72[a]	OK.	OK.
	0.530″	82	39	44,000	38,000	30	60	48	70[b]	OK.	OK.
	0.562″	90	56	49,000	44,500	21	60	48	50[b]	OK.	OK.
	0.625″	96	65	54,000	49,500	16	54	48	33[c]	OK.	OK.
4. 90.18 Cu, 0.50 Te, 9.32 Zn (by diff.).	Annealed	57		39,000	17,000	41	46	56	64[b]	OK.	OK.
	0.562″	89	57	49,500	45,000	17	42	59	25[c]	OK.	OK.
	0.625″	94	64	54,000	49,500	14	42	65	26[c]	broke	@ 100°
5. 90.87 Cu, 0.99 Te, 8.14 Zn (by diff.).	Annealed	54		37,500	12,000	36	37	64	56[b]	OK.	OK.
	0.562″	89	56	48,000	44,000	15	41	76	18[c]	broke	@ 90°

[a] Bent.
[b] Partial fracture (opened at base of notch).
[c] Complete fracture.

RESULTS

Copper-zinc-tellurium.—Analyses and results of tests on the copper-zinc-tellurium alloys are given in Table 1. Hardness and tensile strength are practically independent of the amount of tellurium present, the differences found in such data probably being due to variations in composition or grain size. Ductility, as indicated by elongation and contraction of area in the tensile test, was adversely affected by tellurium. Elongation and contraction of area values for annealed material fell from 54 and 85 per cent for 0 per cent Te to 36 and 37 per cent, respectively, for 0.99 per cent Te, while similar values for the drawn material were correspondingly less.

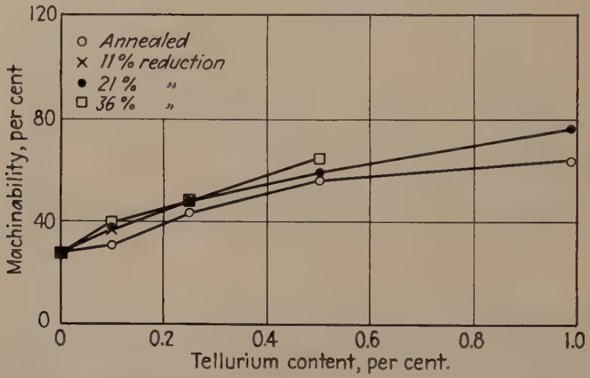

FIG. 1.—RELATIVE MACHINABILITY OF ½-INCH TELLURIUM-BEARING COMMERCIAL BRONZE ROD.

All the rods were successfully bent through an angle of 135° around a pin of their own diameter, ½ in., with two exceptions. The alloys with 0.50 per cent Te, finished with 36 per cent reduction, broke at about 100°, and the alloy containing 0.99 per cent Te, finished with 21 per cent reduction, broke after being bent through 90°.

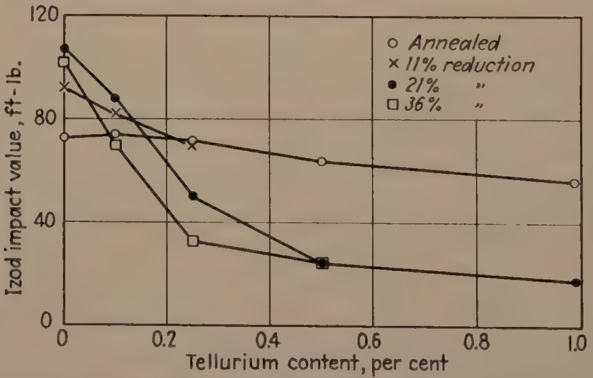

FIG. 2.—IZOD IMPACT VALUES OF ½-INCH TELLURIUM-BEARING COMMERCIAL BRONZE ROD.

The effect of tellurium on machinability of the alloys of this series is shown in Fig. 1. Machinability was found to increase quite regularly with tellurium content. It also increased slightly with reduction of area in drawing, except for the alloy with 0 per cent Te, in which the temper seemed to make practically no difference in relative machinability. Actual figures ranged from 27 to 28 per cent for 0 per cent Te to 56 to 65 per cent for 0.50 per cent Te, and to 64 to 76 per cent for 0.99 per cent Te.

The impact specimens that had been subjected to test were divided into three classifications: (1) those completely broken; (2) those only partly fractured, in which the metal at the base of the notch had opened; and (3) those merely bent, with no opening of the metal at the base of the notch. The less tough specimens, of course, were those that were partly or completely fractured. The toughness of these alloys decreased as the tellurium content increased, and also as reduction of area in drawing increased, except for the lighter draws of the alloys containing 0 and 0.10 per cent Te. The specimens for these two alloys were not actually broken in the test, and the energy required to bend the specimens to allow the striking hammer to pass actually increased for the smaller reductions. The test, therefore, is not the best for such very tough alloys. Fig. 2 illustrates the course of the impact values as functions of tellurium content, impact energy ranging from 107 ft-lb. to 18 ft-lb.

TABLE 2.—*Properties of Tellurium-bearing Tin-bronze Rods, ½-inch Diameter*

Alloy No.	Temper as Drawn from	Rockwell Hardness		Tensile Strength, Lb. per Sq In.	Yield Strength, (½ Per Cent Elong.), Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Contraction of Area, Per Cent	Relative Machinability, Per Cent	Izod Impact, Ft-lb.	Bends	
		F	B							90°	135°
6. 98.30 Cu, 1.58 Sn.	Annealed	69		43,500	15,000	50	77	37	84[a]	OK.	OK.
	0.530″	86	49	46,500	39,000	38	75	38	110[a]	OK.	OK.
	0.562″	94	65	53,500	48,500	25	74	39	110[a]	OK.	OK.
	0.625″	98	71	59,000	53,500	22	70	41	92[a]	OK.	OK.
7. 98.41 Cu, 1.42 Sn, 0.10 Te.	Annealed	63		41,500	15,000	50	69	58	79[a]	OK.	OK.
	0.530″	85	48	45,000	38,000	34	55	62	85[b]	OK.	OK.
	0.562″	94	63	51,500	47,000	21	54	61	75[b]	OK.	OK.
	0.625″	96	67	56,500	51,500	18	60	69	62[b]	OK.	OK.
8. 98.52 Cu, 1.33 Sn, 0.25 Te.	Annealed	60		41,500	16,000	45	61	94	74[a]	OK.	OK.
	0.530″	86	49	45,500	37,500	37	62	89	82[b]	OK.	OK.
	0.562″	94	63	51,500	46,000	22	57	85	60[b]	OK.	OK.
	0.625″	97	66	56,500	52,500	18	54	94	43[b]	OK.	OK.
9. 98.08 Cu, 1.33 Sn, 0.48 Te.	Annealed	56		41,000	17,000	41	47	120	63[b]	OK.	OK.
	0.530″	84	46	44,500	36,000	31	47	127	43[c]	OK.	OK.
	0.562″	92	62	50,500	46,000	20	46	124	26[c]	OK.	OK.
	0.625″	94	63	56,000	51,500	14	42	132	17[c]	OK.	OK.
10. 97.79 Cu, 1.54 Sn, 0.95 Te.	Annealed	64		42,000	14,500	36	39	135	56[b]	OK.	OK.
	0.562″	93	63	52,000	47,000	16	38	137	13[c]	OK.	OK.
	0.625″	97	66	58,500	54,500	11	29	142	9[c]	OK.	OK.

[a] Bent.

[b] Partial fracture (opened at base of notch).

[c] Complete fracture.

In connection with the effect of tellurium on toughness, mention should be made of the toughness of leaded brass. The Izod impact value for commercial free-cutting brass, such as used for comparisons of machinability in this investigation, is approximately 11 ft-lb. for specimens of the given dimensions.

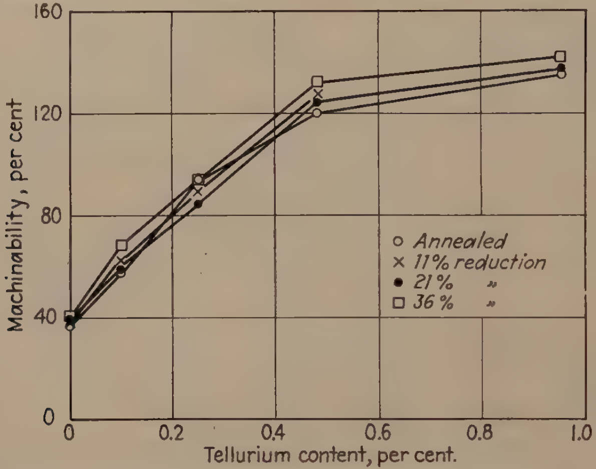

FIG. 3.—RELATIVE MACHINABILITY OF ½-INCH TELLURIUM-BEARING 1.5 PER CENT SN BRONZE ROD.

Copper-tin-tellurium.—Data for this series are given in Table 2, and machinability and impact strength are plotted as functions of tellurium content in Figs. 3 and 4. As with the copper-zinc-tellurium alloys, it is probable that differences in hardness and tensile strength for a given nominal temper were due to slight variations in composition or treatment, and, therefore, the values have not been plotted here. As might be expected, the effects of tellurium in these alloys were similar to those in the copper-zinc-tellurium alloys, differing only in degree.

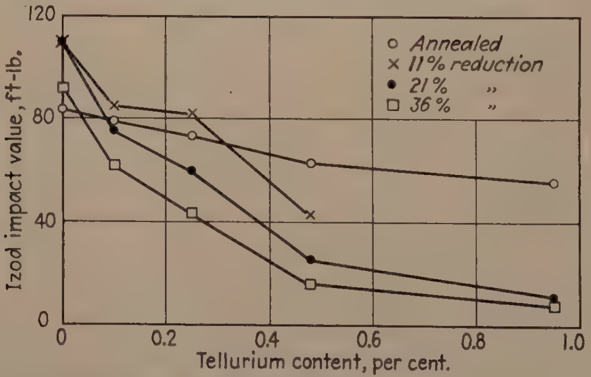

FIG. 4.—IZOD IMPACT VALUES OF ½-INCH TELLURIUM-BEARING 1.5 PER CENT SN BRONZE ROD.

Relative machinability values increased rapidly from 37 to 41 per cent for 0 per cent Te to 120 to 132 per cent for 0.48 per cent Te, then less rapidly to 135 to 142 per cent for 0.95 per cent Te. As before, machinability increased somewhat with hardness of rod. The improvement in machinability in this series was the greatest found in the investigation.

The Izod impact values decreased as tellurium content increased, and were of about the same magnitude as for the copper-zinc-tellurium alloys, the specimens exhibiting the same manner of fracture or partial fracture, depending on tellurium content and temper. The actual figures ranged from a maximum of 115 ft-lb. for 0 per cent Te to a minimum of 9 ft-lb. for 0.95 per cent tellurium.

TABLE 3.—*Properties of Tellurium-bearing Olympic Bronze Rods, ½-inch Diameter*

Alloy No.	Temper as Drawn from	Rockwell Hardness		Tensile Strength, Lb. per Sq. In.	Yield Strength (½ Per Cent Elong.), Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Contraction of Area, Per Cent	Relative Machinability, Per Cent	Izod Impact, Ft-lb.	Bends	
		F	B							90°	135°
11. 96.12 Cu,	Annealed	89		62,500	24,000	54	74	42	113[a]	OK.	OK.
3.14 Si,	0.530″	105	85	72,500	50,000	37	73	42	130[a]	OK.	OK.
0.74 Zn	0.562″	108	90	83,500	58,000	26	67	39	114[a]	OK.	OK.
(by diff.).	0.625″	110	94	94,000	62,000	21	65	38	71[c]	OK.	OK.
12. 95.70 Cu,	Annealed	86		62,000	23,000	53	63	74	99[a]	OK.	OK.
3.13 Si,	0.530″	103	83	75,500	47,500	34	60	72	56[b]	OK.	OK.
0.92 Zn,	0.562″	106	88	84,000	55,000	22	58	67	32[c]	OK.	OK.
0.25 Te	0.625″	110	92	101,000	61,500	12	40	66	24[c]	OK.	OK.
(by diff.)											
13. 95.55 Cu,	Annealed	85		61,000	27,000	46	45	92	78[b]	OK.	OK.
2.63 Si,	0.562″	106	88	82,500	54,000	14	36	81		OK.	OK.
0.45 Te,	0.625″	109	90	98,500	65,000	8	24	77		OK.	OK.
1.36 Zn											
(by diff.).											
14. 96.20 Cu,	Annealed	84		62,000	28,500	43	41	92	43[c]	OK.	OK.
2.72 Si,	0.530″	100	79	69,500	49,000	28	41	86	30[c]	OK.	OK.
0.68 Te,	0.562″	106	88	81,500	55,000	16	38	82	27[c]	OK.	OK.
0.40 Zn	0.625″	109	91	97,500	63,000	9	30	78	6[c]	OK.	OK.
(by diff.).											

[a] Bent.
[b] Partial fracture (opened at base of notch).
[c] Complete fracture.

Elongation and contraction of area fell off with increasing tellurium in a manner similar to the preceding group of alloys. Rods of all tellurium contents and tempers were successfully bent through an angle of 135°.

Copper-silicon-zinc-tellurium.—Test results for the tellurium-bearing copper-silicon-zinc alloys are listed in Table 3, and the effects of tellurium on machinability and impact strength are shown in Figs. 5 and 6. As before, hardness and strength values were found independent of tellurium content.

Relative machinability improved as tellurium content increased to 0.45 per cent, the alloy containing 0.68 per cent Te exhibiting no higher machinability. Actual values ranged from 38 to 42 per cent for 0 per cent

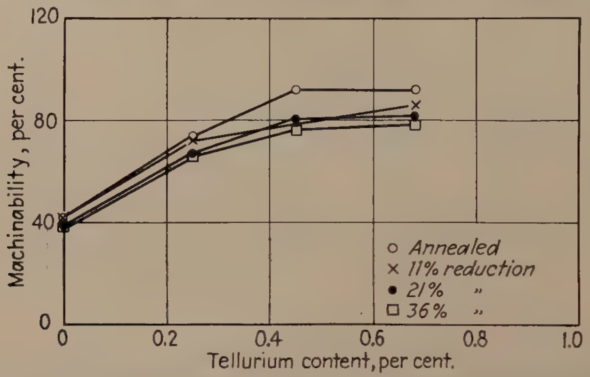

FIG. 5.—RELATIVE MACHINABILITY OF ½-INCH TELLURIUM-BEARING 3 PER CENT SI BRONZE ROD.

Te to 77 to 92 per cent for 0.45 per cent and 0.68 per cent Te. In this series of alloys, contrary to findings in the other two series, machinability decreased as hardness or reduction by drawing increased.

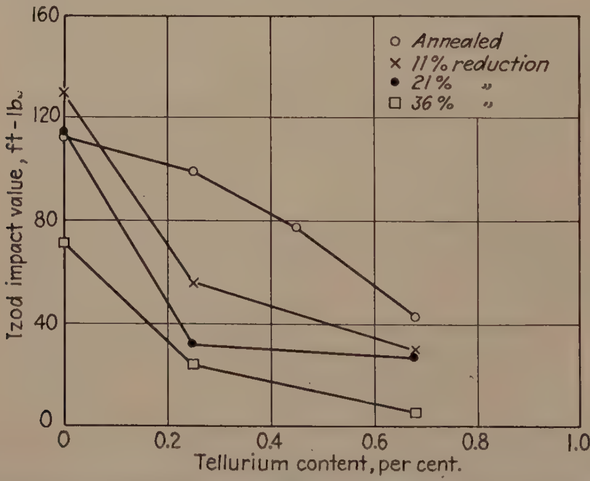

FIG. 6.—IZOD IMPACT VALUES OF ½-INCH TELLURIUM-BEARING 3 PER CENT SI BRONZE ROD.

As expected, the presence of tellurium resulted in decreased toughness and ductility, as indicated by the impact and tensile tests. Izod impact values decreased from a maximum of 130 ft-lb. for 0 per cent Te to a minimum of 6 ft-lb. for 0.68 per cent Te. Elongation and contraction of area of the annealed material dropped from 54 and 74 per cent to 43 and 41 per cent, respectively, for the same range of tellurium content.

Ductility was sufficiently great, however, to permit satisfactory bending of the rods of all tempers through 135°.

Microstructure

Published data on the effect of tellurium on conductivity of copper indicate some degree of solubility, copper containing 0.10 per cent Te being reported to have a conductivity of about 98.5 per cent as compared with 100 per cent conductivity for 0 per cent Te.[3] Solubility of tellurium in the alloys considered here must be very slight indeed, for a bluish gray second phase, presumably a telluride, was readily distinguished under the microscope for tellurium contents as low as 0.10 per cent.

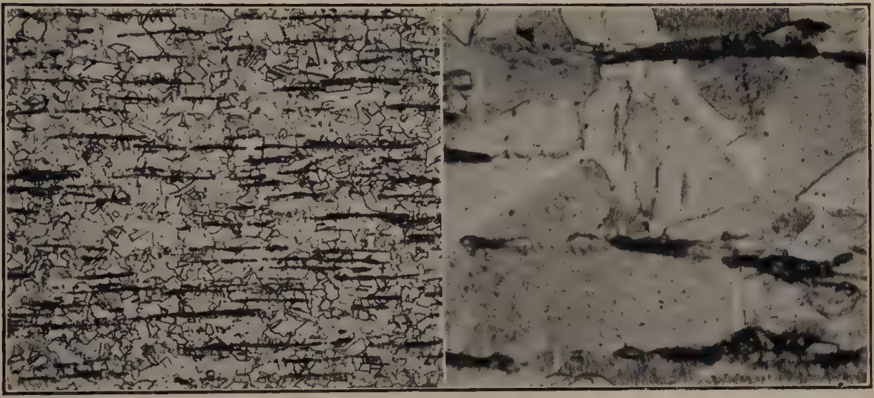
Fig. 7. Fig. 8.

Fig. 7.—Annealed rod; 97.79 per cent Cu, 1.54 Sn, 0.95 Te. × 100.
Fig. 8.—Annealed rod; 98.08 Cu, 1.33 Sn, 0.48 Te. × 750.
Both etched with ammonia and peroxide.

Figs. 7 and 8 show the microstructures of longitudinal sections of annealed copper-tin-tellurium alloys. Structures of the alloys of the other groups are similar in appearance. It is to be noted that the particles of the second phase are distinctly elongated. The improved machinability of the tellurium-bearing alloys, of course, is due to the distribution of the tellurium in this second phase, after the manner of lead-bearing copper alloys.

Summary

Results of tests on drawn rods of tellurium-bearing commercial bronze (90 Cu, 10 Zn), 1.5 per cent tin bronze, and 3 per cent silicon bronze, show that machinability, as determined by a saw-cut test, is distinctly increased by the addition of tellurium. Hardness and strength are practically unaffected within the range of tellurium contents studied, while, as might be expected, toughness and ductility are decreased.

The effect on machinability of added tellurium is greater in the 1.5 per cent tin bronze than in the commercial bronze or silicon bronze. Relative machinability values for the tin bronze increase from about 40 per cent for 0 per cent Te to about 125 per cent for 0.5 per cent Te, and to about 140 per cent for 0.95 per cent Te. Values for commercial bronze increase from about 28 per cent for 0 per cent Te to about 70 per cent for 1 per cent Te, while the values for the silicon bronze increase from about 40 per cent to about 80 per cent for 0.5 to 0.7 per cent Te.

ACKNOWLEDGMENT

The writers wish to make due acknowledgment to Dr. D. K. Crampton, Director of Research of the Chase Brass & Copper Co., for his interest in the work, and to those who may have participated in the investigation in any way.

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DISCUSSION

[For discussion, see page 334.]

Copper Alloys Containing Sulphur, Selenium and Tellurium

BY CYRIL STANLEY SMITH,* MEMBER A.I.M.E.

(Atlantic City Meeting, October, 1937)

FOR many years sulphur and its congeners selenium and tellurium have been regarded as very harmful elements in copper and copper-rich alloys. Like many similar prejudices, this has been found to be partly wrong. All three of these elements actually have no great effect on the working properties of copper and its alloys, and are desirable additions in that they considerably enhance the machinability of alloys in which they are present. Because of their possible commercial importance, a study of the machinability and other properties of the pure binary alloys was made, as described in this paper, and the effect of selenium on a large number of copper alloys was determined.

The current opinion regarding the deleterious effects of elements in this group undoubtedly arose because of occasional failures of tough-pitch copper containing unusually high tellurium, and because of the well-known fact that sulphur causes spewing and unsoundness in tough-pitch copper. Siebe,[1] also Deretchey and Margolina,[2] studied the effect of sulphur on copper and showed that in the absence of oxygen it was present in the form of copper sulphide, which was less harmful to the properties than an equivalent amount of copper oxide. No data have been published on selenium and tellurium, although the statement is often made, following Eggleston,[3] that tellurium makes copper hot-short. Copper specifications call for only traces of these elements. Skowronski and Mosher[4] give data on the effect of selenium and tellurium on the conductivity of tough-pitch copper. In private communication Mr. Skowronski says that the samples were hot-forged from small castings and drawn to 0.081 in. diameter, but it should not be inferred from this that these elements are harmless to the working properties of wirebars and commercial shapes.

CONSTITUTION AND MICROSTRUCTURE

Constitution.—Sulphur, selenium and tellurium exist in their alloys with copper in the form of copper sulphide, selenide or telluride. These compounds are practically insoluble in the solid state and possess limited

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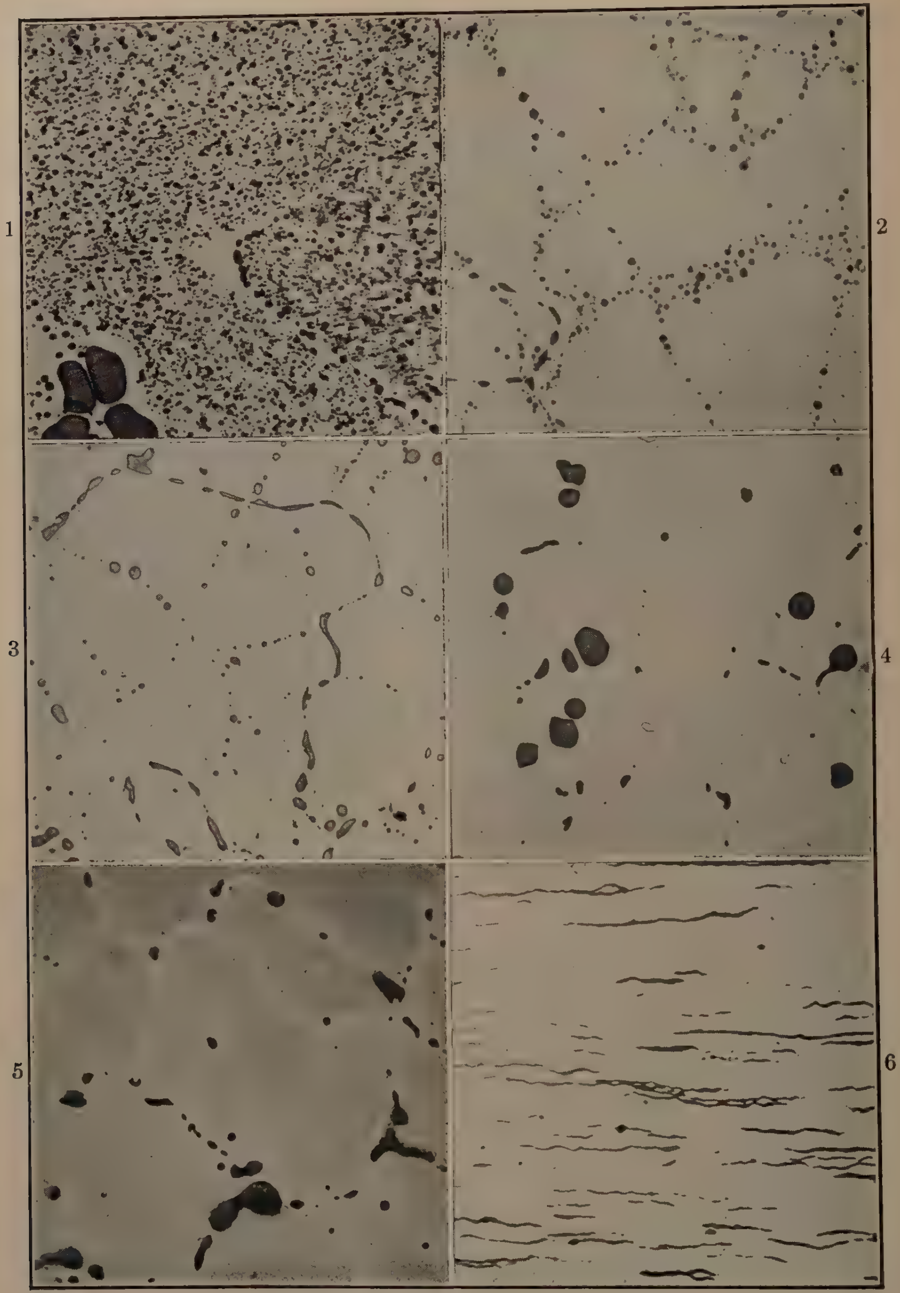
Manuscript received at the office of the Institute Oct. 27, 1937.

* Research Metallurgist, American Brass Co., Waterbury, Conn.

[1] References are at the end of the paper.



FIGS. 1–6.—FOR CAPTIONS SEE OPPOSITE PAGE.

miscibility in the liquid state. The constitution diagrams have been studied by Bornemann and Wagemann,[5] Friedrich and Leroux,[6] and Chikashige,[7] from whose work the data in Table 1 are taken.

TABLE 1.—*Constitution*

Element	Eutectic		Maximum Solubility in Liquid State, Per Cent	Melting Point of Compound, Deg. C.	Percentage of Element in Cu_2X	Reference No.
	Composition, Per Cent	Temperature, Deg. C.				
Sulphur.....	1	1073	2	1155	20.1	5
Selenium....	1	1065	10	1113	38.4	6
Tellurium...	3	1055	(3)	870	50.1	7

All these investigators were more interested in the middle of the diagram and the copper-rich corner was very approximately determined. New analyses made to determine the maximum solubility of these elements in molten copper, at a temperature of about 1200° C., show that molten copper saturated with and in contact with the various compounds contains 1.55 per cent sulphur, 4.11 per cent selenium and 18.15 per cent tellurium.

Microstructure.—The microstructure of the alloys of copper with sulphur and selenium consists of a eutectic with or without primary copper or compound, depending on the composition (Figs. 1 and 2). The appearance is almost identical with that of the copper copper-oxide system. The alloys with tellurium (Fig. 3) show a much coarser "eutectic" and form continuous strings around the grain boundaries. This difference undoubtedly is due to the fact that the second phase when it appears in equilibrium with copper is not solid, as in Cu_2S and Cu_2Se, but is liquid and forms at a monotectic rather than a eutectic point. Because of the low melting point of Cu_2Te and its tendency to form stringers around the grain boundaries, tellurium is rather more harmful to the hot-working properties of alloys than is selenium or sulphur.

The addition of a third element to alloys of copper with elements of the sulphur group will sometimes result in the elimination of the latter ele-

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FIG. 1.—COPPER CONTAINING 0.78 PER CENT S. AS CAST. × 400.
Etched with potassium bichromate, sulphuric acid and sodium chloride applied with a cotton swab.

FIG. 2.—COPPER CONTAINING 1 PER CENT SE. AS CAST. × 400. UNETCHED.

FIG. 3.—COPPER CONTAINING 1 PER CENT TE. AS CAST. × 400. UNETCHED.

FIG. 4.—COPPER ALLOY CONTAINING SI 2.96, S 0.58 PER CENT. AS CAST. × 400. UNETCHED.

FIG. 5.—COPPER ALLOY CONTAINING NI, 19.59; ZN, 4.88; SE, 1.06 PER CENT. AS CAST. × 400.
Etched with potassium bichromate, sulphuric acid and sodium chloride applied with a cotton swab.

FIG. 6.—COPPER ALLOY CONTAINING: SN, 7.38; S, 0.49 PER CENT. COLD-ROLLED TO 0.080 IN., ANNEALED 16 HR. AT 800° C. AND COLD-ROLLED TO 0.01 IN. × 400. UNETCHED.

ments by the formation of insoluble compounds, which float out of the molten alloy on account of the lower density. As would be expected from the decreasing electropositive character of these elements with increasing atomic number, sulphur is the most readily eliminated of the three elements, and tellurium the least. In the presence of 40 per cent zinc, only 0.2 per cent selenium can be retained, but at least 0.6 per cent tellurium remains, and probably more. Practically no sulphur remains in a copper alloy containing 40 per cent zinc, and the addition of even as little as 0.2 per cent zinc will cause some elimination of sulphur. If the third metal does not eliminate the element of the sulphur group it often results in a coarsening of the particles in the eutectic (Fig. 4), and often changes their color or even produces inclusions of a duplex nature (Fig. 5).

Figs. 7–9.—For captions see opposite page.

Casting and Working

The preparation of copper alloys containing sulphur, selenium and tellurium presents no particular difficulties. It is advisable to make the additions as copper sulphide, selenide or telluride, although tellurium may be added as the element, since it is not volatile at the melting point of copper. The compounds are readily made by charging into a warm crucible a mixture of copper turnings with the proper amount of sulphur, selenium or tellurium. Once started, the reaction will proceed rapidly, resulting in a coherent mass that can be melted and cast into suitable form for use.

No data are available on the influence of tellurium and selenium in the presence of oxygen; as, for example, in tough-pitch copper. Ductile castings can be made, perfectly sound and with a deep shrink, by merely melting the alloys under charcoal and pouring out of contact with air, or by deoxidizing and pouring in the usual way. It is important, however, that the deoxidizer be not one with an extreme affinity for sulphur, such as, for example, calcium.

The presence of inclusions of Cu_2S, Cu_2Se and Cu_2Te does not interfere with either the hot-rolling or cold-rolling of copper alloys, except in rare cases. The particles are plastic both hot and cold and elongate on rolling in much the same manner as the piece as a whole. A typical structure of an alloy after cold-rolling to a reduction of 88 per cent is shown in Fig. 6, which is interesting for showing clearly the effect of slip in the adjacent grains on the inclusions. Hot-rolling gives smoother, straighter stringers.

The stringers of inclusions can be broken up and spheroidized by long annealing. Fig. 7 shows an alloy containing 0.6 per cent selenium, 20 per cent nickel, 1.0 per cent zinc, balance copper that has been hot-rolled to 0.08 in. and cold-rolled to 0.04 in. The progressive breaking up of the stringers is clearly shown in Figs. 8 and 9, which are photomicrographs of specimens annealed at 850° C. for 30 min. and 22½ hr., respectively.

Mechanical and Electrical Properties

A series of alloys containing up to 1.0 per cent sulphur, 1.5 per cent selenium, and 2.5 per cent tellurium was made by melting cathode copper under charcoal in a laboratory induction furnace and bottom-pouring out of contact with air after the appropriate addition. The entire lot of castings was hot-rolled in a commercial rod mill from 3-in. dia. to 0.625 in. and then cold-drawn in a single pass to 0.5-in. dia. (36 per cent reduction of area). All the castings rolled perfectly and no hot shortness was observed. The tensile properties, electrical conductivities and machinability are shown in Table 2 and further data on machinability is summarized in Figs. 10–12.

Except for a curiously high drop with the first addition in each case (probably associated with the presence of impurities subsequently removed from solution on larger additions), the conductivity of the alloys is approximately lineally related to the *volume* percentage of the com-

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Fig. 7.—Copper alloy containing approximately: Ni, 20.0 per cent; Zn, 4.0; Se, 0.5 per cent. Hot-rolled from 0.6 to 0.08 in., and cold-rolled to 0.04 in. × 400.

Fig. 8.—Same as Fig. 7, annealed 30 min. at 850° C. × 400.

Fig. 9.—Same as Fig. 7, annealed 22½ hr. at 850° C. × 400.

All etched with potassium bichromate, sulphuric acid and sodium chloride applied with a cotton swab. Samples cut longitudinally.

TABLE 2.—*Properties of Copper Alloys Containing Sulphur, Selenium and Tellurium*[a]

Alloy No.	Composition, Per Cent	Cold-drawn					Annealed 1 Hr. at 600° C.				
		Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 1.4 In.	Conductivity, I.A.C.S., Per Cent at 20° C.	Machinability,[c] Per Cent	Yield Strength,[b] Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 1.4 In.	Conductivity, I.A C.S., Per Cent at 20° C	Machinability,[c] Per Cent
1601	99.990 Cu	50,700	52,100	21.4	99.7	15	8,700	32,500	60.0	102.1	22
1616	0.15 S	49,600	52,200	14.3	97.8	24	8,100	32,800	53.6	99.3	20
1602	0.23 S	51,400	52,500	15.0	97.6	33	7,800	33,000	51.4	99.6	21
1611	0.54 S	52,500	54,300	12.1	95.1	41	9,000	33,600	50.7	96.7	81
1608	0.78 S	56,500	56,500	7.9	91.6	45	11,000	34,800	45.7	92.5	70
1613	0.97 S	53,100	56,700	8.6	90.9	45	11,100	34,900	45.7	91.4	70
1614	0.11 Se	51,200	53,200	19.3	98.9	38	8,400	32,800	57.1	99.0	35
1603	0.26 Se	51,600	53,000	15.7	98.0	64	8,900	32,500	55.7	100.1	63
1607	0.48 Se	50,900	53,600	15.7	97.4	89	8,000	32,800	52.9	98.8	112
1606	1.01 Se	49,900	53,400	11.4	94.4	95	8,500	33,300	48.6	95.6	140
1609	1.44 Se	52,000	54,200	10.0	92.0	91	10,100	33,200	42.1	94.4	150
1615	0.10 Te	50,700	53,100	15.0	99.5	29	7,900	32,800	53.6	99.8	30
1604	0.25 Te	51,500	53,400	14.3	99.9	45	7,900	33,000	54.3	100.6	45
1610	0.45 Te	50,700	53,100	11.4	98.2	58	8,100	33,000	51.4	99.9	72
1605	1.05 Te	51,200	53,300	10.7	97.1	91	8,300	33,200	41.4	98.0	126
1612	2.42 Te	51,100	54,600	7.1	94.5	91	8,800	33,300		96.1	134

[a] These alloys were hot-rolled from 3 in. to 0.625 in., annealed and cold-drawn to 0.5 in. in one pass. Gauge length of test pieces (0.357-in. dia.) was 1.4 inches.

[b] Yield strength is the stress causing 0.5 per cent extension under load.

[c] Machinability is expressed as a percentage of the machinability of leaded brass, measured by the drill test.

pounds present in the copper. The relation holds for all three elements since the compounds are equally insoluble and of comparatively low conductivity. In terms of weight percentages, sulphur has the greatest and tellurium the least effect on the conductivity.

The tensile strength of copper is slightly increased by the presence of sulphur, selenium or tellurium, sulphur having the greatest effect. There is a corresponding reduction in the ductility as measured by the elongation. In no case, however, are the alloys brittle. The property conferred on copper-base alloys by the addition of sulphur, selenium or tellurium most likely to find commercial utilization is the high machinability of such alloys, unaccompanied by hot-shortness, as in alloys containing lead.

A series of crude tests was made to determine the machinability by counting the number of turns of a "standard" 0.25-in. drill required to penetrate 0.25 in. transversely into a rod of the alloy under test under various loads. The drills were replaced at the first signs of wear, and the results from each drill proportionately corrected to the basis of "standard" readings on leaded brass. A typical group of curves showing load versus

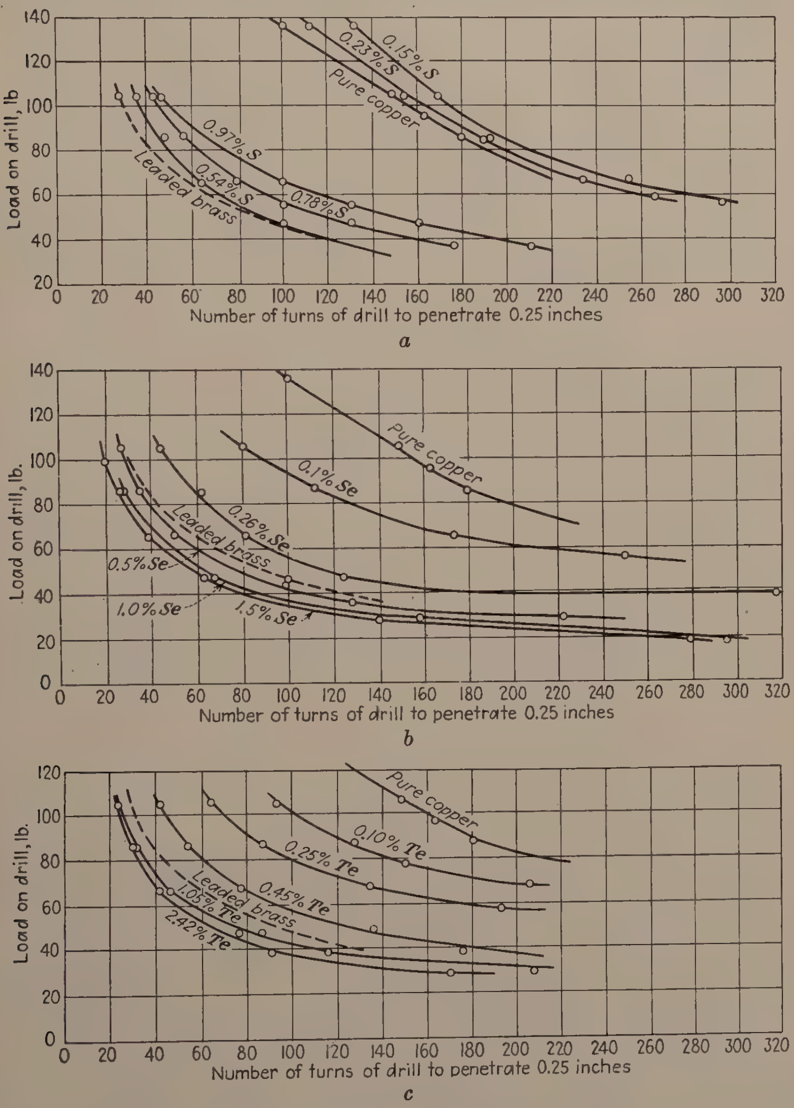

FIG. 10.—CURVES SHOWING MACHINABILITY OF VARIOUS ALLOYS OF COPPER WITH SULPHUR, SELENIUM AND TELLURIUM.

number of turns is given in Fig. 10. These figures include a curve to show the comparison of the alloys with a commercial free-cutting brass of the following nominal composition: copper, 62.0; zinc, 35.0; lead, 3.0.

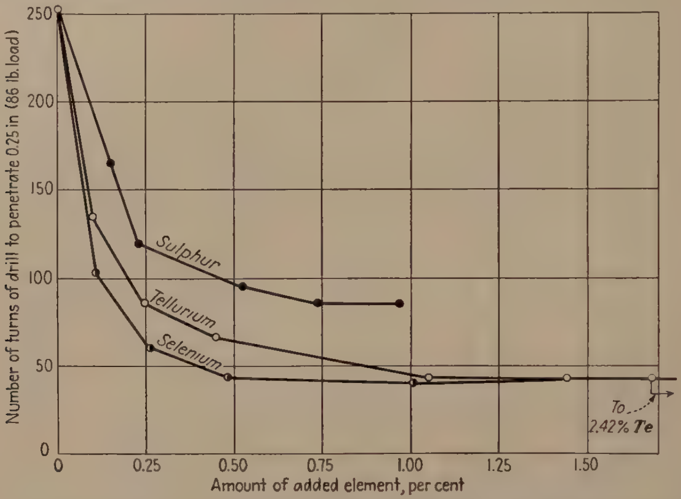

Fig. 11.—The effect of sulphur and its congeners on the machinability of copper (hard-drawn).

Fig. 11, in which is plotted against composition the number of turns of the drill at a constant load (86 lb.) needed to make the standard hole, shows that in hard-drawn alloys the addition of small quantities of any

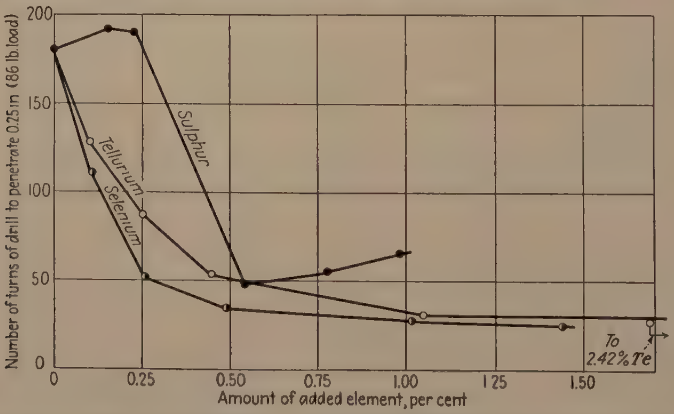

Fig. 12.—The effect of sulphur and its congeners on the machinability of copper (annealed 600° C.).

of the elements sulphur, selenium or tellurium causes an improvement in the machinability, but that beyond about 0.5 per cent little further improvement is gained. Selenium is the most potent addition in small amounts, and in general is the best to add to copper alloys for improving machinability.

The machinability of the annealed alloys is shown in Fig. 12. Selenium and tellurium have the same effect that they have in the cold-worked alloys, but the action of sulphur is peculiar, in that small amounts actually decrease machinability and rapidly wear the drill. Although the sulphide inclusions serve to break up the chips formed, they do not act as a lubricant in the manner that copper selenide and copper telluride do.

Addition of selenium is not limited to binary alloys. Alloys of copper containing about 3 per cent silicon with 0.5 per cent selenium can be hot-worked and cold-worked almost as readily as selenium-free alloys and have similar tensile properties (with slightly less ductility), but their machinability is approximately three times that of the alloys without selenium.

The addition of selenium to the copper-nickel alloys is particularly attractive. Working with laboratory castings, it has been found possible to hot-roll alloys containing 20 per cent nickel and 0.5 per cent selenium, and alloys with larger amounts of nickel can be cold-rolled. As examples of the properties obtainable, the data in Table 3 are given, and show tensile properties and machinability (as determined by the drill test described above, and expressed as the reciprocal percentage of the number of turns necessary to drill a standard hole in a leaded brass). The alloy in question contained 20 per cent nickel and 1 per cent zinc with additions of selenium as stated.

TABLE 3.—*Tensile Properties and Machinability*

Property	No Addition		0.6 Per Cent Selenium		1.0 Per Cent Selenium	
	Hard	Soft	Hard	Soft	Hard	Soft
Yield strength, lb. per sq. in.	64,500	15,930	64,050	14,455	62,700	14,350
Tensile strength, lb. per sq. in.	69,850	46,490	69,800	46,000	67,400	44,825
Elongation, per cent in 2 in.	18.3	55.4	11	50.0	10	48.5
Reduction of area, per cent	67.6	78.3	42.7	59.3	33.0	52.8
Machinability	14	13	48	58	83	88

SUMMARY

Alloys of copper with small amounts of sulphur, selenium and tellurium have been studied. It is shown that these elements do not cause either hot-shortness or cold-shortness in copper, and that they have comparatively little effect on tensile strength although they slightly reduce ductility. These elements greatly improve the machinability of copper, and provide a desirable addition to almost any copper alloy in which improved machinability is required without the hot-shortness associated with lead additions.

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DISCUSSION

(*S. Skowronski presiding*)

[This discussion refers also to the preceding paper, which begins on page 315.]

C. E. SWARTZ,* Cleveland, Ohio.—Some years ago, while attending the University of Wisconsin, I studied under Victor Lenher. He had a number of patents and had every man available working on chemical properties of selenium and tellurium. At the time of his death, as far as I know, there was no commercial metallurgical application of either element in any large volume. Since that time, considerable interest has been created in selenium and tellurium. Where it originated I, for the moment, do not know.

In connection, however, with the remarks on the machinability and the ductility of selenium and tellurium-containing copper alloys, I should like to pass on one little experience we had with tellurium some years ago. It happened to be at one of the smelters of the American Smelting and Refining Co. Occasionally we got what the operating men chose to call "brittle gold" in the electrolytic gold refinery. Repeated chemical analyses finally showed the presence of a very slight trace of tellurium. That, so far as I know, is the only instance of tellurium causing any trouble in any alloy. However, from that experience the average process metallurgist in the nonferrous industry has come to believe that tellurium is one of the elements that is detrimental when added to any metal or alloy.

At the Cleveland Graphite Bronze Co. we have found some very interesting uses for tellurium. All of our main and connecting-rod bearings today, except the cadmium-base alloys, contain tellurium, and that has been true for some time. In the copper-lead alloy, tellurium was added as an element that would tend to prevent corrosion. In another alloy it is added to prevent or tend to prevent segregation. In a third alloy, perhaps the most interesting one and with which we have had most experience, it is added for the purpose of increasing the fatigue resistance. The curve on that is interesting. It happens to be a babbitt alloy containing 3.25 per cent copper, 7.5 per cent antimony.

The fatigue studies were made on a symmetrical reverse bend machine, using a short strip with a neck in it to make the specimen fail at a predetermined point. We plot fatigue against tellurium content, which gives a curve that shows a maximum lying at 0.10 to 0.20 per cent tellurium.

Just exactly what the mechanism of this is, I am not prepared to say, except that we have found that the addition of tellurium to babbitt alloys allows us to produce a much more uniform structure and maintain a grain-size control that is very difficult, if not impossible, in bearing manufacture.

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* Cleveland Graphite Bronze Co.

One other point may be of interest in case of machining. When this element was first added to our babbitt alloys, something over two years ago, the production men reported difficulty in machining. Our process, which I will not go into at the moment, consists in pouring babbitt onto a strip of steel moving through a machine at the rate of 15 ft. per minute. On cooling, the strip passes through two milling cutters, which mill the strip down to a predetermined gauge size. The milling cutters had been machined for the previous period of use of the machine (some five or seven years) to cut babbitt, which is a very soft and ductile material. The addition of the tellurium reduced very slightly the elongation of the material, increased the brittleness, we might say, very slightly and therefore we had to increase the land on the milling cutters in order to cut this slightly harder material—harder from the standpoint of greater toughness.

Physical tests, tension, compression, and so forth, in the laboratory showed that the addition of tellurium to babbitt decreased the ductility very slightly, did not affect the tensile strength appreciably, did not affect the hardness appreciably, and, I have said, increased the fatigue resistance.

S. Skowronski,* Perth Amboy, N. J.—Supporting Mr. Swartz's gold and tellurium, Eastabrook, about as far back as 1906, published the effect of adding tellurium to fine silver. He found that tellurium in a few parts per million in fine silver caused the silver to become very brittle.

The commerciability of both of these metals is rather interesting. Selenium is altogether out of the rare metal class. Selenium today is sold in quantities the world over, with production and sales of over half a million pounds a year.

E. M. Wise,† Bayonne, N. J.—Now that the ice has been broken to considering elements whose cost is of the order of dollars per pound, I should like to suggest that silver be given consideration as a possible means for securing machinability and better bearing properties in situations where lead, selenium or tellurium are inadequate. Moderate quantities of silver are miscible with many copper-content alloys but its solid solubility is apt to be low, so a major proportion of the silver or silver-rich phase is rejected on solidification and cooling yielding a useful dispersion.

I did a little work on the use of silver to produce machinable alloys about 15 years ago and the indications were favorable. The mechanical properties of silver are of the right order and the solidus temperatures of copper or nickel alloys containing it are considerably above the alloys containing lead; furthermore, the addition of silicon to such alloys should not give rise to the troubles encountered with lead-content alloys.

C. S. Smith.—I have not confirmed the embrittling effect of tellurium on silver described by Eastabrook and referred to by Mr. Skowronski. As a matter of fact, some years ago I hot-forged castings of both fine and sterling silver containing 0.5 and 1 per cent of tellurium and selenium, respectively, and the alloys were cold-rolled into thin strip without failure.

O. W. Boston,‡ Ann Arbor, Mich. (written discussion).—It seems unfortunate that this particular method for establishing machinability ratings was used. From many tests,[9] the drill penetration tests, as indicated in this case by the time in minutes for a standardized ¼-in. diameter drill operating under 94 lb. pressure to penetrate

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* Research Chemist, Raritan Copper Works.

† Metallurgist, International Nickel Co.

‡ Professor, Department of Metal Processing, University of Michigan.

[9] National Metals Handbook (1936) 754.

0.100 in. show a rather poor coordination between the drill penetrating time and drill torque, milling energy per chip, and planing force when each is obtained under standardized conditions. The milling, drilling and planing tests by themselves show frequent diversions from one another, but in general a comparatively satisfactory agreement is maintained.

It would have been interesting to see the machinability ratings of the alloys prepared by the author had other methods been used. The drill penetration test is, of course, the most economical to make regarding time and material and equipment. The writer has found it almost impossible, however, to obtain uniform results with a drill for different grindings. A great deal of time is required to prepare the drill to produce duplicate results in the penetration tests, whereas in the other tests, the machinability ratings may be duplicated easily.

Two other types of machinability tests might give data of interest, providing the size of the specimens permitted such tests, that is, surface finish produced under standardized conditions and tool life. It is felt that new ratings placing the materials in a different order of machinability would be obtained for these tests, and it is doubtful whether they would align themselves with the results obtained by the penetration tests or energy or force tests.

C. S. Smith (written discussion).—I cannot but admit the validity of Professor Boston's criticism of the machinability test employed. However, in an investigation of this nature rapidity of testing and economy of material was considered to be more important than absolute accuracy. Practically, the only factors of importance in any free-cutting copper alloys are tool life and surface finish and this can only be determined by long runs in actual production.

A paper by Broniewski and Lewandowski[8] describes a detailed study of the mechanical and electrical properties of copper with sulphur additions up to 0.75 per cent.

Strain Transformation in Metastable Beta Copper-zinc and Beta Copper-tin Alloys

By Alden B. Greninger* and Victor G. Mooradian,† Junior Members A.I.M.E.

(New York Meeting, February, 1938)

Microscopic examinations of quenched (beta) 60:40 copper-zinc and quenched (beta) 74:26 copper-tin alloys have frequently disclosed long, thin parallel bands or markings within the polyhedral beta grains. Apparently, it has been accepted that these markings are mechanical twin bands, although there is no published account of experimental data that might tend to substantiate this belief for the copper-zinc system, and only meager evidence has been submitted for the copper-tin system.

Johnson[10] commented upon the markings he observed after deforming a quenched brass of 55.6 per cent copper and 44.4 per cent zinc. Clark's papers[4] on the heat-treatment of Muntz metal contain many photomicrographs of markings in beta brass; these she referred to as Neumann bands (inasmuch as repolishing and re-etching failed to remove them) and stated that markings present in Muntz metal as quenched were the result of shock imparted during the polishing operation. Van Wert[18] first suggested that these parallel markings in quenched beta brass (60:40) might be alpha precipitated along certain crystallographic planes of the matrix lattice. He showed that upon reheating the specimens to temperatures below 800° C., obvious precipitation of alpha within the large beta grains first occurred at the markings. In a discussion of this paper, Phillips stated (pp. 505–507) that in his opinion the markings observed by Van Wert were mechanical twins resulting from contraction strains produced during the quenching operation.

In a study of segregate structures in beta copper-tin, Smith[17] observed that in the quenched beta phase (containing 74.92 per cent Cu) parallel bands or markings very similar to those in metastable beta brass could be

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Most of the material presented in this paper has been abstracted from a thesis submitted by V. G. Mooradian in partial fulfillment of the requirements for the degree of Doctor of Science, Harvard University, June, 1937. Manuscript received at the office of the Institute Aug. 24, 1937.

* Instructor in Metallurgy, Graduate School of Engineering, Harvard University, Cambridge, Mass.

† Research Associate in Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

[10] References are at the end of the paper.

obtained as the result of a small amount of deformation. Sufficient strain could be induced merely by scratching a polished surface or by cutting a section with a hack saw. After determining the orientations of two beta grains and plotting stereographically the poles of planes located by the intersection of markings on two surfaces, he concluded that the markings were on {133} of the beta lattice. Although the stereographic proof for {133} was inadequate, Smith's work was of sufficient accuracy to show that the markings were definitely not on {112} (as are the familiar mechanical twins in body-centered cubic ferrite[3]). Smith evidently took for granted that the markings were twins; he made no attempt to verify this assumption.

Obviously there has been a tendency to attribute to markings in body-centered cubic alloys (specifically with reference to the copper-zinc and copper-tin systems) the accepted identity of Neumann bands in body-centered cubic ferrite. It is believed that the present paper, embodying the results of an extensive optical and X-ray study of markings in metastable beta alloys, should demonstrate the fallacy of this assumption.

COPPER-ZINC SYSTEM

MATERIALS

The alloys used in this investigation were supplied by Dr. C. S. Smith, of the American Brass Co., in the form of hot-rolled plates $\frac{3}{8}$ by 4 by 10 in. From these plates specimens, usually about $\frac{3}{8}$ by $\frac{3}{8}$ by $\frac{1}{2}$ in. in size, were prepared and used as the starting point for all heat-treating,

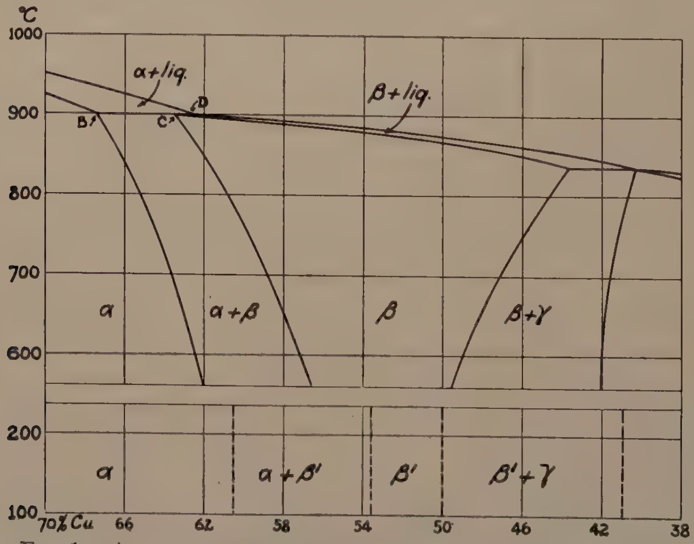

FIG. 1.—A PORTION OF THE COPPER-ZINC EQUILIBRIUM DIAGRAM. Liquidus and peritectic points after Schramm.[16] Solid solubilities after Hansen.[9]

microscopic and X-ray studies. An analysis of the alloys is given in Table 1.

In Fig. 1 is reproduced a portion of the copper-zinc equilibrium diagram, which shows that a 60:40 copper-zinc alloy in equilibrium at room temperature consists almost entirely of alpha. If the alloy is quenched from a temperature above 750° C., the beta phase may be retained, and the amount of alpha present at the beta grain boundaries will depend primarily upon the quenching speed. With ordinary water quenching, the grain boundaries tend to be rather thick with alpha "reeds"; quenching in a 10 per cent solution of NaOH from a temperature of 855° C. produces beta grains with essentially no alpha at the grain boundaries. Accordingly, beta (polyhedral grains) present at room temperature in a 60:40 alloy is in a metastable condition, as contrasted with beta in a 52:48 alloy, which is stable at all temperatures.

CRYSTALLOGRAPHIC PLANE DELINEATED BY MARKINGS IN METASTABLE BETA BRASS

Preparation of Specimens.—The solution heat-treatment was carried out with the specimen attached to a thin wire suspended within a vertical tube furnace equipped with automatic temperature control. For a furnace temperature of 855° C., the time at temperature was about three minutes, total time in the furnace about five minutes. Quenching was done by plunging the specimen into a 10 per cent NaOH solution. The average grain size after this treatment was 3 to 5 mm. Specimens usually were polished (on three sides) through 000 paper before heat-treatment, with additional polishing preceding the deformation and microscopic examination, except for studies of quenching-markings, when all polishing was done before heat-treatment.

TABLE 1.—*Analysis of Copper-zinc Alloys*

Constituent	Composition, Per Cent	
	60:40 Alloy	52:48 Alloy
Copper	60.78	51.89
Zinc	39.21	48.10
Lead	0.003	0.001
Iron	0.010	0.011
Cadmium	0.002	0.002

Various kinds of deformation were tried in attempts to produce markings that would facilitate subsequent orientation studies. Best results were obtained from slight compressive deformation, like that produced by squeezing in a vise. Observations made from the microscopic study of deformed specimens may be summarized as follows:

1. In metastable copper-zinc, small amounts of deformation produce two kinds of surface effects having visibly different characteristics: (1) sets of long, thin parallel markings, and (2) a furrowlike striated relief in some grains. The latter is difficult and, in many instances, impossible to see with ordinary vertical illumination, but is readily visible with oblique illumination. These deformation bands are considerably broader (10 to 50 times) than the first markings that appear, and have more irregular boundaries and directions. After repolishing and re-etching, they disappear but the markings remain.*

2. With increasing amounts of deformation (up to 2 or 3 per cent reduction in thickness) broad markings appear in positions formerly occupied by deformation bands. Additional markings, both thin and broad, become visible (Figs. 2 and 3). The broad markings have a definite, fine structure, which consists of narrow markings at an angle with the direction of the broad markings.

3. The markings are plates of varying depths and thickness; the broad markings often extend throughout the entire volume of a beta grain. After careful etching (with $H_2O_2 + NH_4OH$) the markings take on a characteristic brown to dark blue color, which contrasts strikingly with the lemon yellow background of beta brass.† Overetching will destroy this color (as well as the fine structure in the broad markings) and the markings will appear black.

4. Markings do not appear in every grain of a specimen that has been deformed. Even after heavy deformation (about 5 per cent) certain grains may be covered and discolored with markings (Fig. 4), while the surface of some neighboring grains will be merely warped and buckled, possibly furrowed but still having the characteristic lemon yellow color of beta brass.

5. Markings never maintain the same direction across a grain boundary; that is, they are related in some way to the beta lattice.

6. It was impossible to produce markings in 52:48 (stable beta) specimens, even in those that had been given the same treatment as had the 60:40 specimens. However, abundant slip lines and deformation bands were formed.‡

Many specimens of metastable beta copper-zinc were found to contain markings when examined immediately after quenching in 10 per cent NaOH (Fig. 5). No markings were observed after water quenching; however, only a few water-quenched specimens were examined critically before deformation. Markings produced as a result of quenching also had the characteristic dark brown to blue color of deformation markings, but were always rather narrow and considerably straighter and more regular than those obtained by mechanical deformation. They did not extend very far below the surface and usually could be removed by a repolish beginning with 00 paper. The perfection of these markings is well illustrated in Fig. 5.

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* Strictly speaking, both of these surface effects fall within the category of "markings." As data are presented, it will become increasingly apparent that a more descriptive term is needed for the striated banding, which is referred to as "marking" throughout this report.

† This change in color may often be seen even before etching.

‡ These will be described and analyzed in a future publication dealing with the deformation of 52:48 beta copper-zinc.

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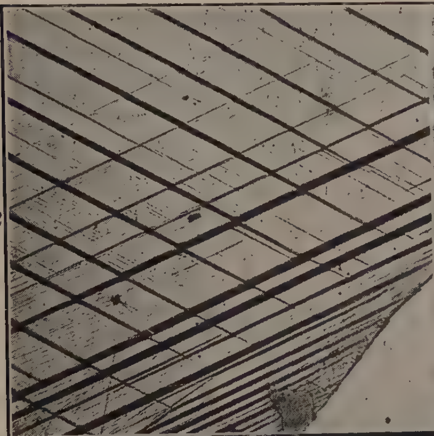

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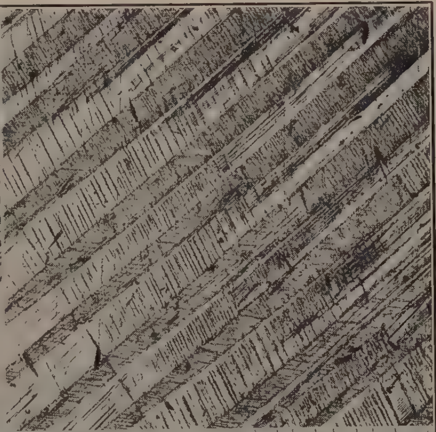

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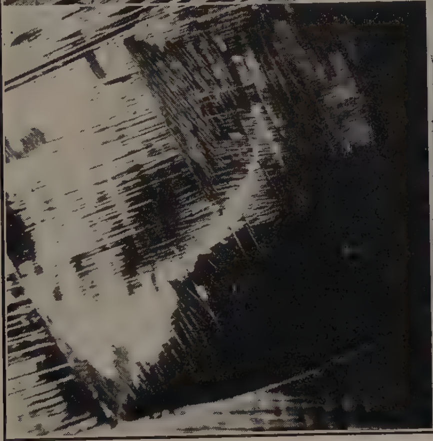

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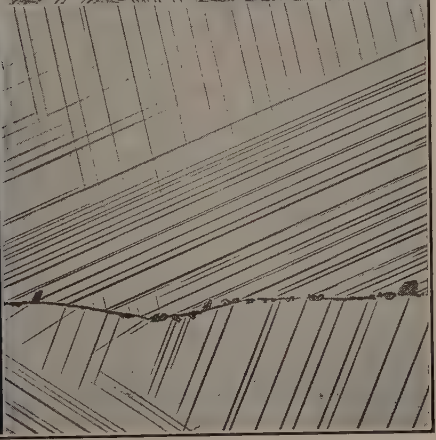

Figs. 2 and 3.—Markings in deformed metastable beta copper-zinc. Vertical illumination.

Fig. 2, heavy etch × 75; Fig. 3, light etch × 200. Etched with $NH_4OH + H_2O_2$.

Fig. 4.—Markings in heavily deformed metastable beta copper-zinc. Limited-azimuth dark-field illumination. × 15.

No polishing or etching after deformation. Compare with Fig. 10.

Fig. 5.—Markings in metastable copper-zinc as quenched. Vertical illumination. × 75.

Etched with $NH_4OH + H_2O_2$.

Orientation Study.—Through the use of a microscope equipped with an illuminator capable of giving various combinations of light-field and dark-field illumination, it was a simple matter to trace markings from one surface over the edge to another surface (at approximately right angles to the first one). Thus, by working with two surfaces, it was possible to locate poles of planes delineated by markings[2] with reference to the orientation of the matrix grain projected stereographically. By means of the back-reflection Laue X-ray method,[6] the beta grain orientations were determined with respect to one surface of polish and the common edge, and each orientation was plotted on a 15¾-in. stereographic projection together with the marking poles pertaining to that particular grain. The angles between the polished surfaces on each specimen were measured with an optical goniometer. The over-all inaccuracy in the determination of orientation and the location of marking poles is estimated at about 1°; most of the poles of quenching markings are undoubtedly located to within 0.5°.*

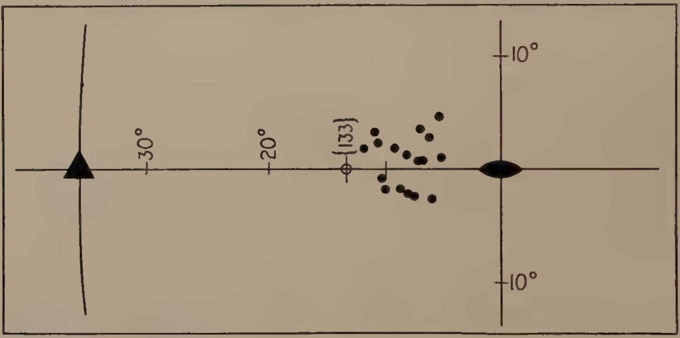

FIG. 6.—STEREOGRAPHIC PROJECTION OF MARKING POLES IN COPPER-ZINC PLOTTED ON STANDARD {110} OF THE BETA LATTICE.

Only center region of standard projection is shown. Poles from quenching markings are plotted in lower quadrant; poles from deformation markings in upper quadrant. Oval = $\{110\}_\beta$; triangle = $\{111\}_\beta$.

Results.—Some 25 or more marking poles were located stereographically. The results obtained from all grains from many different specimens were the same: The planes delineated by markings agree with no principal crystallographic plane of the beta lattice. Marking poles deviate from $\{110\}_\beta$ by from 4.5° to 11°; the average deviation, or the mean position, is at 6° to 7° from {110}, which position is approximately $\{155\}_\beta$ to $\{166\}_\beta$. Typical results obtained from the analysis of markings are shown stereographically in Fig. 6; the upper quadrant contains poles of deformation markings (from five grains in two different specimens), and the lower quadrant poles of quenching markings. It may be seen that so far as orientation is concerned there is no difference between markings obtained from quenching and those obtained by mechanical deformation.

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* The accuracy of operations was tested by locating the twinning planes of a large twinned crystal of copper available in the laboratory. All three twinning-plane poles located by means of twinning-plane traces deviated less than 0.5° from the equivalent poles located by X-ray patterns.

In addition to the statements above, the following observations concerning the habits of markings were made during the course of the orientation study:

1. Parallel sets of markings characteristically occur in pairs, one on each side of the pertinent $\{110\}_\beta$. That is, considering the stereographic region about $(110)_\beta$, if markings are present corresponding approximately to $(\bar{5}51)_\beta$, markings corresponding to $(5\bar{5}1)_\beta$ will also be present in most cases. However, even in a pair of this sort the individual deviations of each set of parallel markings from $(110)_\beta$ may differ by as much as 6°.

2. For any given set of parallel markings obtained from quenching, individual markings (throughout the entire area of a beta grain) are practically always parallel to within the limit of measurement, which for the microscope used in this work was about 0.2°. Deformation markings (logically enough) often deviate as much as 1° from parallelism.

3. Fine structure markings present "within" the broad ones produced by heavy deformation are related to the beta lattice in the same way as are all other markings.

IDENTIFICATION OF MARKINGS IN METASTABLE BETA COPPER-ZINC

Methods of Study.—Use was made of X-ray diffraction analysis of both powders and single crystals in an attempt to follow and evaluate the physical changes that occur as a result of the deformation of metastable beta brass.

Small single crystals (about 1 by 1 by 3 mm.) were cut, with a fine jeweler's saw, from large grains of quenched 60:40 brass. The crystals were deeply etched, and X-ray diffraction patterns were then obtained in a rotating-crystal camera, using copper radiation, before and after successive amounts of deformation. Deformation was accomplished by squeezing with pliers, and the first deformation given each crystal was roughly comparable to that received by the specimens used in the orientation study. Microscopic examination of all these crystals showed that the deformations produced abundant markings on the surface.

The powder method was applied to filings taken from the original 60:40 alloy. The filings were sealed in evacuated Vitreosil tubes and heated to 855° or 860° C. The quenching operation was carried out in such a way that the Vitreosil tube was shattered the instant it reached the quenching medium, thus allowing direct contact between the filings and the quenching bath (10 per cent NaOH). Filings quenched in this manner gave diffraction patterns showing only traces of alpha.* The powders of metastable beta were then cold-worked various amounts and diffraction patterns were taken after each deformation. Light deformation was produced by passing a 1-in. diameter steel roll (using only the weight of the roll) over the powders spread out on a smooth glass plate, and the heaviest deformation by hammering in a steel mortar.

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* Diffraction patterns obtained from filings quenched without breaking the Vitreosil tube showed about equal intensities of alpha (f.c.c.) and beta (b.c.c.) lines.

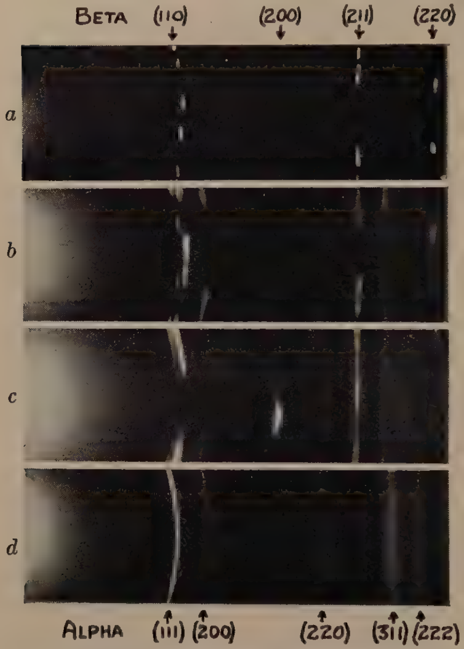

FIG. 7.—SEGMENTS OF ROTATING CRYSTAL PATTERNS OF METASTABLE BETA COPPER-ZINC, BEFORE AND AFTER DEFORMATION, SHOWING TRANSFORMATION FROM PURE BETA TO DISTORTED ALPHA STRUCTURE.

Copper radiation, filtered. *a*, single crystal; *b*, same crystal after slight deformation; *c*, another crystal after slight deformation; *d*, latter crystal after heavy deformation.

Results.—Metastable beta brass after slight amounts of deformation gives diffraction patterns containing lines which do not belong to the body-centered cubic beta structure; that is, an actual lattice transformation occurs as a result of the deformation.* This transformation is in the direction b.c.c. → f.c.c.; it does not proceed *directly* from b.c.c. to f.c.c. but takes place in a series of "steps" involving one or more transition lattices. The transformation may be arrested and the transition lattices thereby made evident, because of the fact that the transformation is a function of deformation, i.e., proceeds with it; and, of course, the degree of deformation may be varied at will. After slight cold-work, lines of the transition lattices become evident and with increasing amounts of deformation some of these lines disappear; the remaining ones shift and gradually merge into a face-centered cubic pattern. At the same time, the body-centered cubic beta lines become more and more faint and finally disappear completely. Table 2 contains a summary of data obtained from several X-ray films selected for measurement. Results from the study of single crystals and filings are essentially in agreement, although it was found that the rotating crystal patterns were more sensitive in detecting weak transition-lattice lines.

Of the 11 new lines obtained after light deformation, eight may be accounted for by a face-centered tetragonal (f.c.t.) lattice† of $a = 3.76$

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* Patterns of deformed stable (52:48) beta copper-zinc merely show broadening of the b.c.c. lines.

† For the original b.c.c. beta lattice, $a_0 = 2.930$. For the f.c.c. alpha lattice present in the quenched filings $a_0 = 3.687$.

and $c/a = 0.96$ (Table 2). Of the three lines unaccounted for,* one (line 2) is relatively strong and appears in every pattern of lightly deformed single crystals and filings; the other two lines (lines 7 and 9, relatively weak) were detected in only one-third of the patterns. After moderate deformations, lines 2 and 7 are not present; line 9 is merged with line 8 to form one broad {311} line. The eight "f.c.t. lines" become somewhat broader and shift position with increasing deformation (except line 10, which disappears). The shift is toward a smaller parameter and larger axial ratio. First and second order {111} do not shift; they maintain the same *d* values for all degrees of deformation.

Table 2.—*Transition-lattice Lines on X-ray Patterns of Deformed Metastable Copper-zinc*

d VALUES IN ÅNGSTROMS

Line No.	Indices	Single Crystals		Filings, Light Deformation[a]	Calculated Values for Face-centered Tetragonal Lattice ($a = 3.76$; $c/a = 0.96$)
		Light Deformation[a]	Medium Deformation[a]		
1	{111}	2.13	2.13	2.14	2.14
2		1.96		1.975	
3	{200}	1.88	1.87	1.875	1.88
4		1.79	1.80	1.800	1.80
5		1.330	1.320	1.330	1.33
6	{220}	1.288	1.297	1.304	1.30
7		1.233			
8		1.129	1.128	1.130	1.130
9	{311}	1.113	1.110[b]	1.115	
10		1.094			1.096
11	{222}	1.065	1.064	1.068	1.071

[a] Average values from three films.

[b] {311} line on each film is about 2 mm. broad; parameter calculated assuming parameter spread equivalent to 1.4 mm.

Low-temperature Transformation of Metastable Beta Brass

In the early stages of this research, during an investigation of the possible effect of low temperatures upon marking habits, it was discovered that the mirrorlike qualities of polished surfaces of metastable beta brass specimens were markedly altered by immersion in liquid air. A striated effect was produced, imparting to each grain a pronounced oriented sheen. The striations persisted for a few seconds after the specimen was removed from the liquid air, then gradually faded and eventually disappeared as the specimen temperature increased. Because of the apparent resemblance between these markings and those produced by deformation, it was deemed advisable to study in more detail their habits and identity.

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* Attempts to fit all new lines into one lattice were unsuccessful.

Microscopic Study of Low-temperature Markings.—The low-temperature microscope stage constructed for this study is shown diagrammatically in Fig. 8. The apparatus consists of a vacuum-tight bakelite chamber with a glass top, a copper rod extending through the bottom for heat transfer. The polished specimen and thermocouple were wedged into a hole at the top of the copper rod (within the chamber) and the chamber was evacuated through a liquid-air trap. The specimen was then cooled by dipping the copper rod into the low-temperature mixture (solid CO_2 + alcohol, followed by liquid air).* The specimen was observed through a microscope during the cooling cycle; thus it was possible to see the actual formation and growth of markings as they appeared on the surface. The time required to reach the lowest temperatures ranged from 5 min. to 1 hr., depending upon whether the cycle was being observed or photographed; behavior at all speeds was essentially the same.

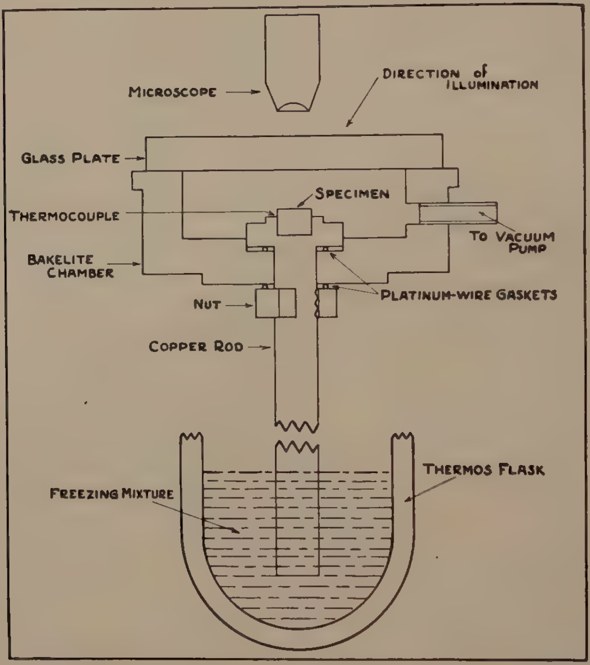

FIG. 8.—DIAGRAMMATIC SKETCH OF LOW-TEMPERATURE MICROSCOPE STAGE.

Observations made from many cooling cycles on several different specimens may be summarized as follows:

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* The lowest specimen temperature for all runs was about −130° C.

1. Markings are formed only in metastable beta brass; they do not appear in stable (52:48) beta brass.

2. Markings are formed only while the specimen is cooling and they disappear progressively as the temperature rises (to room temperature). That is, no new markings appear during an interval in which the specimen is maintained at a fairly constant low temperature (say, at −100° C.). If the temperature is then lowered, new markings appear; if it is raised, some markings disappear.

3. There are no critical temperatures for the formation of markings during cooling. The first few scattered markings become evident at temperatures between −30° and −40° C.; these are short and thin and usually originate at grain boundaries (Fig. 9). As the temperature decreases, these markings grow in length (toward the interior of the grain) and at the same time other markings appear. The formation and growth of markings is not strictly continuous, but is by a process of instantaneous increments whose periods are dependent upon the speed of cooling.

4. Low-temperature markings are rendered visible by virtue of the relief which their formation imparts to the surface of the specimen; hence, the quality of their photographic image is dependent upon the direction and quality of illumination. The photographs in this section were taken with oblique illumination of about the quality of limited-azimuth dark field. With diffuse vertical illumination, the image more closely resembles that of a fully martensitic structure.

5. If a specimen of metastable beta brass is subjected to several low-temperature cycles, the formation of markings appears to become increasingly sluggish and increasingly lower temperatures are required to produce equivalent structures. A few permanent faint markings are usually visible (at room temperature) in a specimen that has undergone repeated cooling. For a given grain, the network of markings produced by the first cooling is identical, in so far as surface geometry is concerned, with networks obtained in subsequent coolings.

Crystallographic Plane Delineated by Low-temperature Markings.—Polished specimens of large-grain metastable (60:40) beta brass were photographed at low temperature to preserve a record of markings with respect to a reference line on the surface. Grain orientations were then determined at room temperature (see p. 342) and plotted stereographically together with trace-normals of the markings registered on the photograph. The lattice perfection of the beta grains was unaffected by the cooling cycle (or cycles); consequently, the accuracy attained in this analysis should be comparable to that in the study of quenching markings (see p. 342), although here it was possible to locate only traces instead of poles.

Low-temperature markings are oriented with respect to the beta lattice in the same way as are markings produced by quenching or mechanical deformation. Trace-normals deviate from $\{110\}_\beta$ by from

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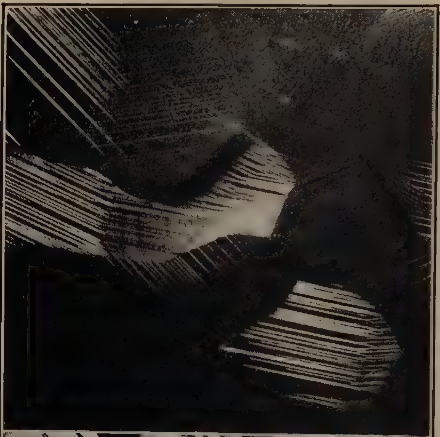

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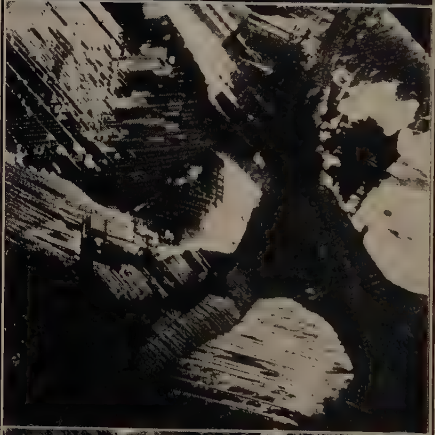

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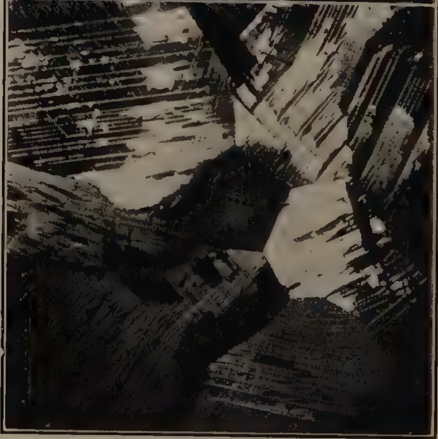

FIG. 9.—EARLY STAGE IN LOW-TEMPERATURE TRANSFORMATION OF METASTABLE BETA COPPER-ZINC. OBLIQUE ILLUMINATION FROM ONE LAMP. × 10. Photograph taken at about −50°C.

FIG. 10.—METASTABLE BETA COPPER-ZINC AT LOWEST TEMPERATURE REACHED BY LIQUID-AIR COOLING. ILLUMINATION SAME AS FIG. 9. × 10.

FIG. 11.—SAME SPECIMEN AREA AND CONDITIONS AS FIG. 10, EXCEPT DIRECTION OF ILLUMINATION CHANGED.

5° to 10°; actual deviations, measured from $(110)_\beta$ to the point where the trace-normal crosses $[1\bar{1}0]_\beta$, were as follows: 5°, 9°, 6.5°, 8°, 6°, 8°, 9.5°, 6°, 8.5°, 6°, 6.5°, 7.5°.

Identification of Low-temperature Markings.—In order to establish whether or not low-temperature markings evidenced the formation of a new lattice, a series of Debye patterns was taken at temperatures approaching that of liquid air. For this work, a low-temperature Debye camera was constructed, similar in basic design to the microscope stage previously described. The specimen, consisting of minus 200-mesh filings, was mounted on thread in the usual manner and sealed with collodion in a small hole at the tapered end of the copper rod. The chamber was evacuated through a liquid-air trap and the copper rod was kept immersed in liquid air during the exposure; no attempt was made to measure temperatures. The traces of frost formed on the specimen gave no trouble; only the first five lines of ice were present on low-temperature patterns.

TABLE 3.—*New Lines*[a] *Present in Low-temperature X-ray Patterns of Metastable Beta Brass, Compared with Those in Patterns of Deformed Single Crystals*

d VALUES IN ÅNGSTROMS

Low-temperature Patterns	Deformed-crystal Patterns, Light Deformation	Low-temperature Patterns	Deformed-crystal Patterns, Light Deformation
?	2.13	1.18	
1.96	1.96	1.145	
1.87	1.88	1.132	
	1.79	1.095	1.094
1.33	1.33	1.068	1.065
1.29	1.29	0.872	
1.24	1.23	0.859	
	1.13	0.853	
	1.11	0.835	

[a] Some of the lines recorded may be doublets.

The results of this study were conclusive in establishing the presence of a new lattice (or lattices) in metastable beta brass at near liquid-air temperature. The transformation does not occur in stable (52:48) beta brass. One specimen of metastable beta was subjected to six consecutive cooling cycles and all of the six low-temperature patterns showed the presence of the "transition lattice" lines, whose intensity was roughly equal to that of the beta lines also present. Room-temperature patterns taken after each cooling showed only the body-centered cubic beta lines together with traces of alpha that was present in the original quenched sample.

The general spottiness of the X-ray lines seriously interfered with attempts to determine the structure of the new lattice.* However, the line measurements that could be made are presented in Table 3. Most but not all of the new lines on low-temperature patterns agree well with those that appear on patterns of deformed crystals.

COPPER-TIN SYSTEM

With a few exceptions, all of the experiments on beta copper-zinc described in the previous section were duplicated with beta copper-tin.

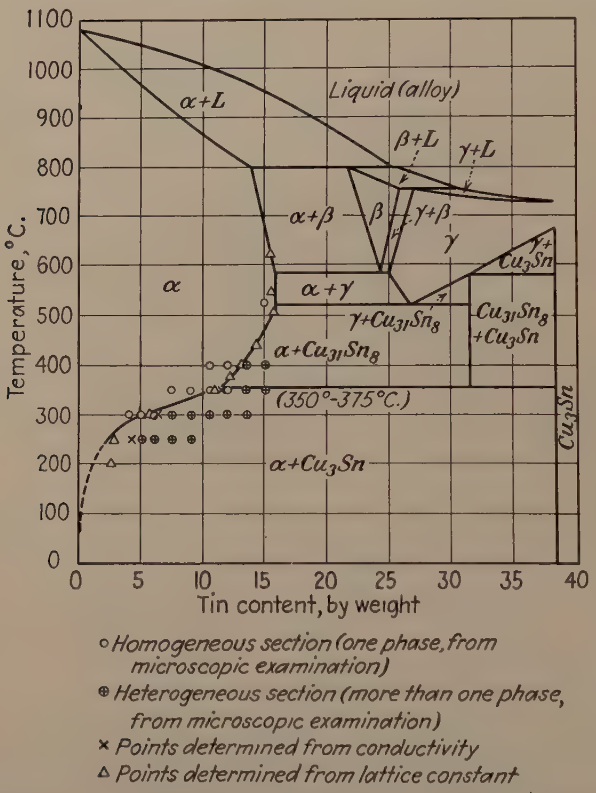

FIG. 12.—PORTION OF COPPER-TIN EQUILIBRIUM DIAGRAM. AFTER HAASE AND PAWLEK.[7]

Except for the preparation of specimens, experimental methods for both alloys were practically identical.

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* The improvement in patterns that would obtain from the use of a low-temperature camera designed to permit specimen rotation should materially simplify this task.

An alloy containing 25.6 per cent tin[*] and 74.4 per cent copper was prepared from pure tin[†] and a master alloy[‡] containing about 23 per cent tin and only 0.07 per cent of reported impurity (silicon), and was used in all subsequent studies. The alloy was melted in a graphite crucible, stirred, and then allowed to cool slowly in the crucible in order to obtain a coarse grain structure. Small specimens prepared from this ingot were quenched from 700° C. in various media; a water quench was sufficiently effective completely to suppress the low-temperature phases.

Crystallographic Plane Delineated by Markings in Metastable Beta Copper-tin

Formation of Markings.—Abundant markings were present in specimens quenched from 700° C. (Figs. 13 and 14), especially those quenched in the 10 per cent NaOH solution. Markings are readily produced in metastable beta copper-tin by deformation, but they are usually short; furthermore, because of the alloy's brittleness, it is difficult to deform a specimen without breaking it. Consequently, deformation markings were studied only to the extent of establishing that they were parallel to

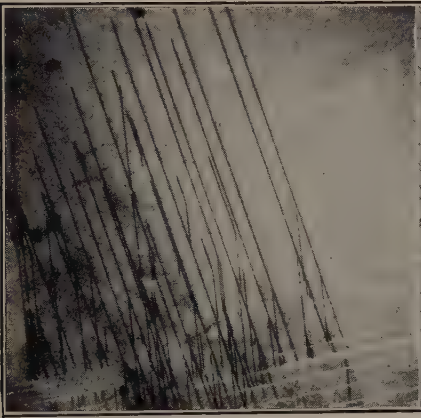

Fig. 13.

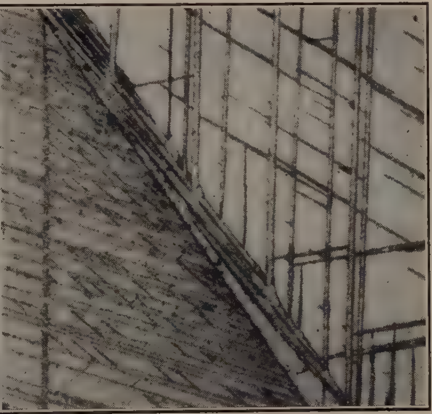

Fig. 14.

Fig. 13.—Markings in metastable beta copper-tin as quenched. Limited-azimuth dark-field illumination. × 30.
No polishing after quenching. Etched with dilute HNO_3.

Fig. 14.—Markings in metastable beta copper-tin as quenched. Vertical illumination. × 650.
Polished after quenching and etched with dilute HNO_3.

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[*] In alloys containing less than 25 per cent tin, the beta phase cannot be preserved at room temperature by quenching from the beta range; the as-quenched structure of these alloys is "martensitic" (Hansen, p. 639).

[†] Furnished by the International Tin Research and Development Council; 99.97 per cent.

[‡] Furnished by Dr. C. S. Smith, of the American Brass Company.

quenching markings, and the latter were used in all orientation studies.

Results.—All poles of planes delineated by quenching markings in metastable beta copper-tin were very close to $\{133\}_\beta$. The eight poles located with maximum accuracy showed the following deviations from $\{133\}_\beta$: 0.5°, 2.5°, 1°, 1.5°, 2°, 2°, 0° and 1°. The deviations from $\{133\}_\beta$ were all in the direction of the adjacent $\{110\}_\beta$, a fact that, in view of the small deviations involved, may or may not be significant.

Identification of Markings in Metastable Beta Copper-tin

Filings taken from the copper-tin ingot were quenched from 700° C., then cold-worked various degrees, and diffraction patterns were taken after each deformation (for details, see p. 344). The resulting patterns conclusively established that deformation produced a lattice transformation, the most noticeable changes appearing in X-ray patterns taken after only slight amounts of deformation. The new lines were diffuse and no attempt was made to measure them systematically. The set of lines is completely different from the transition lattice lines on patterns of deformed metastable beta copper-zinc; furthermore, after heavy deformation, all lines, including the body-centered cubic beta lines, are so diffuse as to be scarcely visible.

No markings were produced by liquid-air cooling of metastable copper-tin.

Discussion

The results of this investigation establish that the markings present in deformed (or as-quenched) metastable beta copper-zinc and beta copper-tin, formerly believed to be mechanical twins, are in reality manifestations of lattice transformation. It has also been shown, at least for the copper-zinc alloys, that a similar, probably the same, transformation occurs during cooling to liquid-air temperature.*

Recently, Kaminski and Kurdjumow[11] announced that a face-centered tetragonal transition lattice was found in copper-zinc alloys of zinc content "between 40 and 44 per cent." The new lattice was evidently obtained as a result of quenching, and the authors state that quenched alloys of "composition near the alpha-phase boundary" gave X-ray patterns showing nothing but the face-centered tetragonal lattice; the parameters given were $a = 3.755$, $c = 3.586$, $a/c = 1.047$. They also reported a heat effect in the cooling curves of "some alloys" at −14° C.; unfortunately, they do not state whether the X-ray patterns were taken at room temperature or below. The present writers have been unable to confirm completely Kaminski and Kurdjumow's findings. Only lines of the alpha and beta phases were present in room-temperature

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* The possibility that the transformation of beta copper-tin may begin at some lower temperature should be recognized.

X-ray patterns of quenched 60:40 and 62:38 copper-zinc. Furthermore, as has been stated previously, a single face-centered tetragonal lattice cannot account for all of the transition lattice lines detected for this alloy. It should be noted, however, that the parameters of the "face-centered tetragonal" lattice which accounted for eight of the eleven new lines resulting from slight deformation agree well with parameters reported by Kaminski and Kurdjumow.

The orientation habits of copper-zinc markings are indeed difficult to rationalize. Previous orientation studies have, in general, demonstrated that the plates responsible for banded structures on the surface of a specimen are parallel to certain crystallographic planes of the matrix lattice, and that a departure from crystallographic parallelism is logically reflected in a like departure from parallelism between individual bands. For markings in beta copper-zinc, however, the banded structure is perfect but the crystallographic parallelism is surprisingly poor. Moreover, no important lattice plane is even roughly delineated by the markings; the best that can be said crystallographically is that the plates are always at an angle of from 5° to 11° with {110} of the beta lattice and only a few degrees removed from ⟨110⟩ zones.* This necessarily implies that although the locations of these plates are roughly determined by matrix orientation, the growth of markings cannot properly be referred to as a "separation along certain preferred crystallographic planes." Markings in beta copper-tin show much more crystallographic regularity, though it is difficult to understand why a plane such as {133}—more properly {266} in the body-centered cubic lattice—is selected. It should be noted that these markings deviated measurably from {133} and that the deviation was always toward the adjacent {110}.

The phenomenon of strain transformation is, of course, not new. It is a well-known fact that certain austenitic steels readily transform on being cold-worked;[1,5,15] however, the subject has received little systematic study and it is undoubtedly true that transformations of this type are considerably more common than has hitherto been supposed. The transformation is important in relation to metallographic studies of alloy systems, for it is quite possible that the presence of this kind of marking in a quenched alloy may be taken to indicate a second phase, whereas in reality it represents a transition lattice, which has no place on a constitutional diagram.

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* The first crystallographic study of the segregation of the alpha from the beta phase as a result of thermal treatment was made by Mehl and Marzke,[14] who state that the alpha phase precipitates in needle form approximately along [111] of the beta lattice, and further conclude that the true direction is most likely to be [556]. Phillips (ref. 14, p. 152) advanced evidence to indicate that a platelike precipitate is more likely and that the plane delineated may be {112}. Hanemann and Schröder[8] suggested that alpha needles have as growth direction [111] of the beta lattice and that the needles are aligned along {111}; the inconsistencies in Hanemann and Schröder's arguments were pointed out by Mathewson and Smith.[13] Weerts[19] concluded that plates are formed by low-temperature precipitation and that these plates are parallel to {110}, high-temperature precipitation producing irregular needles. Weerts' conclusions have been, for the most part, substantiated by Marzke.[12] It should be noted that of all the above studies of the precipitation of alpha from beta, only in the original work of Mehl and Marzke is the possibility recognized that the segregate form may be parallel to no matrix direction or plane of low indices. Further work is needed to determine whether or not the oriented habits of platelike alpha segregate are the same as those of strain-transformation markings.

It is perhaps advisable to comment upon the use of the terms "strain transformation" and "marking" in this report. Admittedly neither of them is adequately descriptive. Unfortunately, the former cannot be improved upon to any great extent until more is known about the motivating force behind these transformations. For metastable beta copper-zinc, the transformation occurs specifically as a result of quenching, plastic deformation, and liquid-air cooling; and although strain is produced in all these operations it may well be questioned whether the transformation is always due to strain. Certainly any dimensional change induced by liquid-air cooling is almost pure contraction. The phenomenon undoubtedly is somewhat constitutional in nature, just as is the martensite transformation, and for terminological purposes it may be unwise to give too much attention to the treatment that initiates the transformation. Nonetheless, there is need for an accepted term that would designate the process, without regard to alloy system, whereby a transition lattice is formed from a metastable solid solution; a general term for the structural constituent is needed also. If present trends (more noticeable in foreign publications) continue, it may be that the term "martensite" will eventually transcend its original meaning and come to signify a structural type in nonferrous alloys as well as steel.

Summary

1. The markings that are present in deformed (or as-quenched) metastable beta copper-zinc and beta copper-tin, formerly believed to be mechanical twins, have been shown to be manifestations of lattice transformation. For copper-zinc alloys, the transformation also occurs during cooling to liquid-air temperatures, giving metallographic structures that are oriented in the same way as those produced by deformation; this low-temperature transformation is reversible.

2. Markings in metastable beta copper-zinc are roughly parallel to $\{155\}_\beta$ or $\{166\}_\beta$; in beta copper-tin, markings are parallel to $\{133\}_\beta$.

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DISCUSSION

(*Jerome Strauss presiding*)

N. AGEEW,* Leningrad, U. S. S. R. (written discussion).—The influence of strain upon the rate and ease of the transformation from the metastable to the stable state has been pointed out long ago and repeatedly. This problem has attracted attention in connection with the process of age-hardening and by determination of the phase boundary on constitutional diagrams.

In spite of the relative remoteness of this problem, the paper by Greninger and Mooradian has much interest. The results presented show clearly that often in studying equilibrium in the solid state it is necessary to take into account the influence of strain, which affects considerably the state of equilibrium in different directions. Many constitutional diagrams can be cited to show that the conclusions of individual investigators differ considerably. One such example is the diagram for magnesium-cadmium alloys, upon which information is very contradictory. Recently, with Mr. A. V. Nazarov, I have investigated these alloys in a range near 25 atomic per cent of magnesium (the complete results will be published shortly in Russian). Our X-ray and microscopical data have shown the existence of two phases, instead of the chemical compound $MgCd_3$, established by Grube, Schiedt and Dehlinger. A homogeneous compound has been decomposed in our investigation into two phases, with magnesium and cadmium-like lattice. The magnesium-cadmium alloys disclose a considerable capacity to form twin and slip bands by mechanical deformation and quenching. It is possible that the different results of examination of the magnesium-cadmium system (Urasow, Hume-Rothery and Rowell, Grube and Schiedt, Dehlinger, Korniloff, Ageew and Nazarov) can be explained by the strain sensibility of these alloys. The strain transformation, as we know, has not been taken into account previously in study of the constitutional diagrams of the magnesium-cadmium alloys, but after this paper such errors should be impossible.

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* Supervisor of the X-Ray Laboratory, Institute of General and Inorganic Chemistry, Academy of Sciences of the U. S. S. R.

The experimental results of this paper do not make it possible to assert the fallacy of the previous assumption about the connection of markings with twin and slip bands. It is most probable that the mechanical deformation (twins and slips) causes the strained places in the crystal lattice at which the superfluous phase commences to precipitate.

From the point of view of transformation of the metastable phase beta into the stable alpha, the results of the experiments with liquid air are not clear. At all temperatures, from room to the lowest the alpha phase is stable, but, as shown by the authors, the process of markings formation is reversible. This process goes not only from the metastable phase to the stable one, but also in the opposite direction. Further research to clarify the nature of this process is very desirable, and important for practical and theoretical metallurgy.

G. Derge,* Pittsburgh, Pa. (written discussion).—Though agreeing that the results of this paper are "indeed difficult to rationalize," I do not despair of the possibility. The similarity of the "transformation markings" of Figs. 2 and 3 to the "deformation bands" of Figs. 3 to 7 of Dr. Greninger's paper on the deformation of beta brass (p. 372–373, this volume) is striking. The likeness of all these figures to the patterns formed in palladium by hydrogen[20] and in quenched aluminum alloys[21] is also very marked. The results from these papers combined seem to go a long way toward explaining all of the patterns mentioned above. The forces that produce the authors' "deformation bands" have created so much disorder in the lattice that these regions are highly reactive and nucleation of the new phase is very easy in these areas. Furthermore, reaction will extend beyond these disordered areas comparatively slowly, especially since the cases under consideration are low-temperature reactions. It is not improbable, as has already been suggested,[20] that such disordered areas propagate themselves, since the volume changes involved in the reaction must set up appreciable local stresses, but in any event the shape of the reacted area should resemble the shape of the deformed area.

Such a viewpoint simplifies the picture appreciably, as it allows us to think that these reactions are operating by simple crystallographic mechanisms such as those that have been so well established for all other types of solid reactions. Thus, the deviations from regularity of pattern, which the authors have measured, are determined by the reaction area rather than the crystallographic mechanism. Such deviations have been well established in other cases and have been discussed adequately elsewhere.[22]

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* Metals Research Laboratory, Carnegie Institute of Technology.

[20] D. P. Smith and G. Derge: *Trans.* Electrochem. Soc. (1934) **66**.

[21] W. L. Fink and D. W. Smith: page 223, this volume.

The deviations of the straight, narrow markings shown in the remaining figures of this paper cannot be so readily explained. However, the Widmanstätten studies to which the authors refer show that the outward form of the new phase does not determine its crystallographic relation to its parent. Until actual orientation relations between the two phases have been determined, there is no basis for abandoning the belief that some exact relation does exist.

F. H. Clark,* New York, N. Y.—The work of Dr. Greninger and Dr. Mooradian in this paper leaves little doubt that these unusual markings do not conform to atomic planes of the beta phase.

The X-ray work that we carried out in 1925 was on a sample that corresponded in general to the treatment given to sample C, Fig. 7. At that time we noted the alpha lines but the beta lines, as we called them then, were too faint for exact measurement. The great improvement in the sensitivity of X-ray diffraction equipment since that time has probably been an aid in the identification of the transition lattice of the metastable beta system.

Regarding the terminology in reference to these markings, I should like to say that as far back as 1926, Mr. Edgar Bain discussed this matter with me and suggested that the precipitation of alpha from a quenced beta structure might very well be comparable to martensite in steel. Since this term has been gradually extended by others, as, for example, the iron-cobalt-tungsten system investigated by Dr. Sykes, it seems reasonable to adopt the term martensite as suggested by the authors in today's paper.

C. H. Samans,† State College, Pa. (written discussion).—The ultimate solution to all of these problems involving lattice transformations, regardless of whether they are of the Widmannstätten type or not, must involve at least two major points: (1) a mechanism whereby the atoms proceed from their initial positions in one lattice to their final positions in the other; (2) a knowledge of the lattice energies or interatomic forces that keep them in these positions and cause them to follow a certain definite procedure in the process of transition instead of taking what might seem to be the most direct path. Concerning the second of these items, not much can be said because we know far too little, except in a very general way, about the factors involved. It would seem that some change in the free energies of the atoms must be important, but whether this will lead us eventually to a new "valence" concept, to a shift in atomic energy levels involving a change in atomic symmetry, or to some as yet unknown factor can only be, at present, pure conjecture.

Concerning the first point, too, the problem seems to be more complicated than would be expected because, on the face of it, it should merely be one in simple straightforward geometry. On this basis what has appeared previously to be a quite satisfactory mechanism has been worked out by J. Weerts.[23] However, the experimental data of Greninger and Mooradian definitely cannot be accounted for by this mechanism and therefore it would seem to require some revision. Since these transformations frequently take place by a strain-free process, it would seem that low index planes and directions in one lattice should be parallel to low index planes and directions in the other, the transformation consisting of simple shears. In many instances this has been shown to be true. However, occasional examples have been found as in the present paper and in several by R. F. Mehl and his co-workers for which serious deviations, much larger than the experimental error, have occurred. These deviations have been most frequently explained by the obvious method of choosing the nearest plane or direction, regardless of its indices, as the "transformation plane or direction." This may be the true solution but some of us prefer to take the viewpoint that these deviations result from the transformation mechanism itself and consequently a careful study of them should give us clues that might be expected to lead to the ultimate solution of the problem.

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[22] G. Derge: *Metals and Alloys* (December 1937) 337.

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† Assistant Professor of Metallurgy, School of Mineral Industries, The Pennsylvania State College.

[23] Ueber Umwandlungsvorgaenge im β-Messing und in β-Silber-Zinklegierungen. *Ztsch. Metallkunde* (1932) **24**, 265.

Let us consider the present paper by way of illustration. The authors have collected many kinds of experimental data but, obviously, since they have failed to present a suitable mechanism to explain these data they have been unable to find one, and so will probably welcome the few suggestions that we can offer. Weerts' proposed mechanism can be best described as taking place in three stages: (1) a shear parallel to the most closely packed plane of the beta lattice, (110), in the direction $[\bar{1}10]$ and of a magnitude of about 0.36; (2) a shear parallel to what was previously a (112) plane of the beta lattice in a [111] direction and of a magnitude of about 0.21; (3) a slight dimensional readjustment to bring the atoms into their face-centered positions in the alpha lattice.

A study of these steps will show that the resulting orientation relationships should be

$$(110)\beta \parallel (111)\alpha$$
$$[111]\beta \parallel [110]\alpha$$

The author's data show a deviation of about 7° from this relationship. Kaminski and Kurdjumow, in their recent paper, also described a face-centered tetragonal structure of the same dimensions as that found by the present authors and explained it by a transformation of the ordered beta phase instead of the disordered phase which would seem to be more probable from the study of the constitutional diagram. The resulting preferred arrangement of the copper and zinc atoms would then give a face-centered tetragonal lattice of the CuAu type. However, as opposed to this hypothesis, the present paper shows quite definitely that for the X-ray patterns of lightly deformed material and for those taken at low temperatures, several extra lines are found that cannot be accounted for by the face-centered tetragonal structure and that, consequently, it is more than probable that an entirely different lattice is found in these specimens, though whether or not it exists alone cannot be stated definitely even though it might be suspected from the completely reversible nature of the low-temperature transformation.

Since the steps in the aforementioned mechanism are vectorial in nature the order in which they occur should be immaterial, so let us consider step 2 as taking place first. In Fig. 15 are shown the atomic arrangements on the (110) plane of the beta lattice in three positions; (*a*) before shearing, (*b*) after shear of 0.21 Å on $(1\bar{1}2)$ planes in the $[\bar{1}11]$ direction, and (*c*) after a specific shear of 0.21 Å on $(\bar{1}12)$ planes in the $[1\bar{1}1]$ direction. In *b* and *c* the light lines represent the original beta lattice and the heavy lines the deformed lattice which, as can be readily seen by a brief consideration of its symmetry, will be monoclinic. This monoclinic lattice will account for all the lines on the author's X-ray patterns but because of its low symmetry it will give, naturally, many additional lines. While most of these will be eliminated by structure factor considerations it is doubtful whether it alone is the lattice that has given the reported patterns. Also, it will not as yet account for the markings. Shear upon (110) has been ruled out by our experimental data as the second step in the transformation but Fig. 15 shows that if shear were to take place on the plane that was previously $(1\bar{1}0)$ of the original beta lattice, and that is normal to the plane of projection, so it appears only as a trace, we would get, as the result of this second step, markings that would lack some 7¼° of being parallel to the $(1\bar{1}0)$ plane of the undeformed beta lattice. This is of the correct order of magnitude and in the proper direction to explain the deviations of the author's markings. Furthermore, it will corroborate their findings in still another way, since they found that "parallel sets of markings characteristically occur in pairs, one on each side of the pertinent {110}." Fig. 15 *b* and *c* shows that the postulated mechanism would give markings of exactly these characteristics, the deviation being positive in one case and negative in the other. Larger or smaller angular deviations can be explained, of course, quite simply by varying the magnitude of the specific shear in step one. It should be made clear that while the plane and direction of shear for this first step are identical with those found by Mathewson and Edmunds for twinning in body-centered cubic metals the magnitude is only one-sixth of that required to give a twinned orientation.

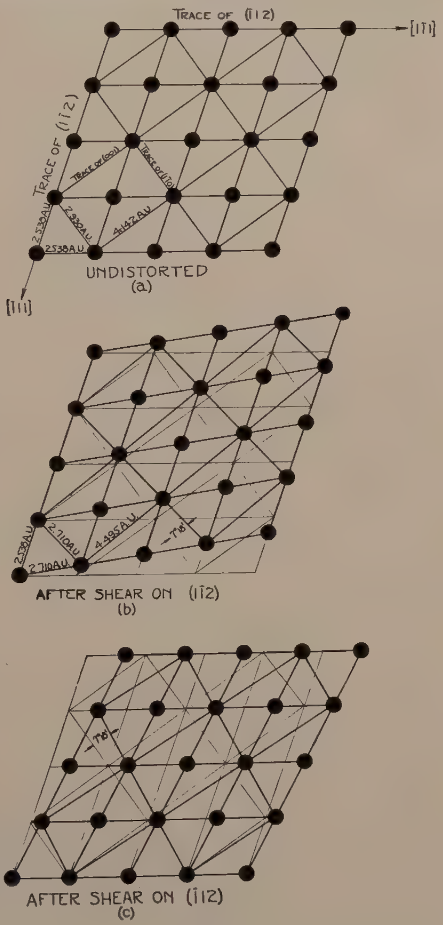

FIG. 15.

It is difficult to say just what the exact nature of this second shearing process is, other than that it seems to be parallel to the indicated plane, probably in what was originally an [001] direction, and of small magnitude. We have not had the opportunity to carry the study further, and in view of the author's X-ray results it did not seem advisable until more precise data were available. However, an orthorhombic lattice with the approximate parameters $a{:}b{:}c = 1.64{:}1{:}1.5$ and $b_0 = 2.60$ will very nearly explain the observed X-ray patterns if the correct structure factors are used, and such a structure can be derived from the monoclinic lattice by a simple shear on the plane and in the direction mentioned previously, provided there occurs simultaneously a contraction of the lattice; i.e., a closer approach of the atoms to each other.

Another interesting sequel to the mechanism suggested above can be found with a little thought. In order to have the markings appear in pairs as found by the authors certain requirements are necessary; e.g., the original shear on {112} planes must occur throughout a rather thick (normal to the plane of projection) "block" of the crystal, adjacent blocks shearing alternately on the two {112} planes, and the second shear must take place over a rather extensive area in order to get plates of transformed material. Such plates would then deviate from $(110)_\beta$ by about 7¼°. On the other hand, if the shears took place only throughout relatively thin layers, the resulting transformed products would appear as "needles" bounded in cross section by $\{112\}$ planes of the original beta lattice and by the realigned $(1\bar{1}0)$ planes of the beta lattice. The long axis, as can be seen from Fig. 16, would be parallel to (111) directions either as they occurred in the original beta lattice or as they were realigned by the first shearing process. If, in adjacent blocks of material, second shear takes place in a restricted manner, as shown in Fig. 16, either one or two pairs of needles can be obtained that will deviate from each other by an angle of about 9°. It will be remembered that R. F. Mehl and O. T. Marzke[24] found that, under some conditions of heat-treatment at least, the precipitated alpha was found in the form of needles, which might have been lathelike in character, occurring in pairs inclined to one another at angles varying from 5° to 12½° with the greatest percentage lying around 8° to 9°. At the time the needles were explained as lying parallel to (556) or a similar direction instead of (111) even though, as was pointed out in the discussion to the paper, this explanation would require needles occurring in sets of three, something that was not observed. If the above suggested steps in the mechanism of the transformation of beta to alpha are correct, the needles of Mehl and Marzke can be explained by the same process as the plates that Greninger and Mooradian have found, the sole differences between the two processes being the extent of the volumes over which the shears take place.

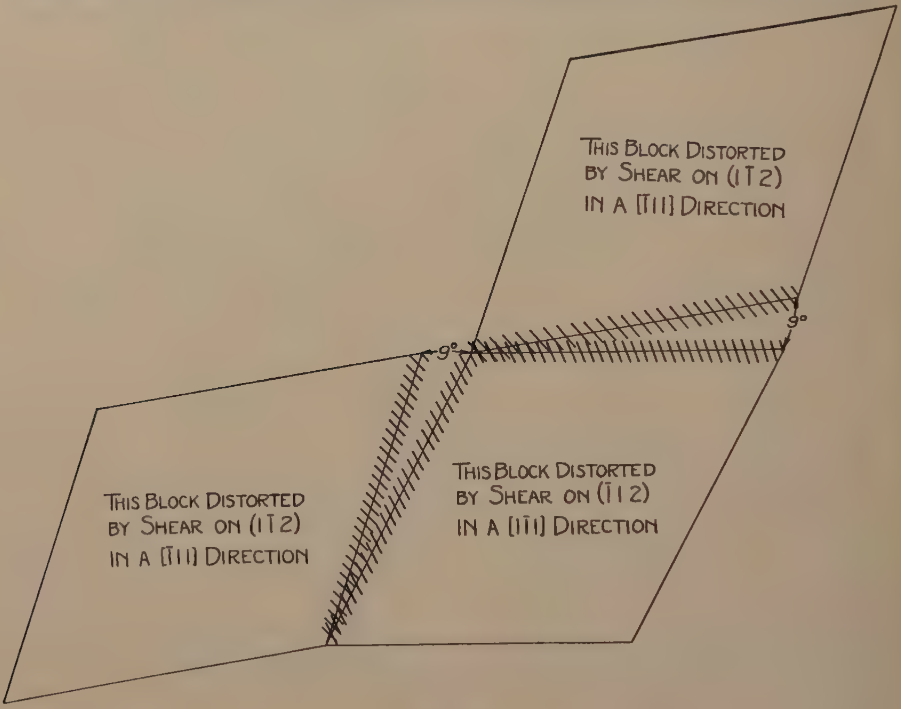
THIS BLOCK DISTORTED
BY SHEAR ON $(1\bar{1}2)$
IN A $[\bar{1}11]$ DIRECTION
9°
9°
THIS BLOCK DISTORTED
BY SHEAR ON $(1\bar{1}2)$
IN A $[\bar{1}11]$ DIRECTION
THIS BLOCK DISTORTED
BY SHEAR ON $(\bar{1}12)$
IN A $[1\bar{1}1]$ DIRECTION

Fig. 16.

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[24] Studies upon the Widmannstätten Structure, II—The Copper-zinc Alloys and the Copper-aluminum Alloys. *Trans.* A.I.M.E. (1931) **93**, 123.

Admittedly the suggestions that have been made above may seem to be far fetched in many instances, but this discussion was not by any means intended to give a complete and established transformation mechanism. Furthermore, the authors, with their more complete data and knowledge of the problem, are in a much better position to determine whether or not the suggestions made have any merit and are likely to prove of assistance in their final solution, something that we sincerely hope they will attempt. The fact that their results indicate that at least a portion of the transformation takes place by a process that is practically strain-free as well as completely reversible argues well for their success in finding a complete mechanism for the transformation. If this can be found, the structures existing in the intermediate steps may be of great assistance in working out and obtaining a solution to the problem of the lattice energies and interatomic forces involved.

C. E. Swartz,* Cleveland, Ohio.—During the past three years, we have been doing some very careful work on the tin-bearing alloys. Those who have worked on these systems realize that the technique of polishing and etching is very difficult. Recently, we have come upon some figures on the etched surfaces which are very close to the type of figures the authors have been discussing this morning. Because of the very difficult technique, we thought it was from some previous operation, but on very deep etching and repolishing, we were able to confirm the fact that the figures involved were other than cold-working from the polishing and etching. So I wish to make the point that it is perhaps a more universal phenomenon than some of us realize. The particular composition of this alloy was 3.25 per cent Cu, 7.5 Sb and the balance tin.

C. S. Smith,† Waterbury, Conn.—There is a point of some practical importance in connection with this interesting and important study of transformation in beta copper alloys. Phillips[25] and later Baker[26] showed that, if an alloy in the narrow composition range (around 62 per cent Cu) where the equilibrium phase is beta at high temperatures and alpha at low temperatures is quenched at a sufficiently rapid rate from a temperature where the alloy is homogeneous beta, the beta will pass directly into a phase that has the metallographic characteristics of alpha. It is certainly neither a marked beta nor the alpha plus beta complex resulting from ordinary quenching. I wonder if possibly the alloy in this condition may contain a massive form of the transitional phase discussed by the authors of this paper, instead of phase centered cubic alpha as has been supposed. Do the authors have any X-ray evidence on this point?

I. Isaitschew,‡ E. Kaminsky‡ and G. Kurdjumow,‡ Dnepropetrowsk, U. S. S. R. (written discussion).—The strain transformations found by Greninger and Mooradian in the copper-zinc alloys belong to the type of transformations that were studied on a number of alloys in our laboratory. On the basis of experimental data we have come to the conclusion that two types of processes take place during the transformations and decomposition of solid solutions.[27] To the first type belong processes the rate of which greatly depends on the temperature, their rate falling practically to zero at a sufficiently low temperature (diffusion processes of redistribution of concentration, usual growth of crystals). Processes of the second type are characterized by the great rate at which they pass in separate lattice regions of the solid solution, independent of the temperature; the development of these processes cannot be prevented even by rapid quenching, as they take place and develop at a great rate also at low temperatures.

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† Research Laboratory, American Brass Co.

[25] A. J. Phillips: *Trans.* A.I.M.E. (1930) **89**, 196.

[26] R. S. Baker: *Trans.* A.I.M.E. (1932) **99**, 159.

‡ Physical Technical Institute.

[27] G. Kurdjumow: General Laws of Phase Transformations in Eutectoid Alloys. *Bull.* de l'Acad. des Sci. U. S. S. R. (1936) No. 2, 271. (In Russian)

Processes of the second type are observed often during transformations in alloys and take place in combination with processes of the first type or in pure form. Transformations of the second type have received the name of "diffusionless," as they develop without any changes in the concentration of solid solutions, or of transformations "by jumps" (*sprunghafte Umwandlungen*) as they develop at a very great rate, or of "martensite transformations," as originally this type of processes was clearly observed during the transformation of austenite into martensite in steels.

The mechanism of this type of transformation consists in a regular rearrangement of the lattice in such a way that the relative displacement of neighboring atoms does not exceed the interatomic distances and the atoms do not interchange places. This mechanism of the process clearly explains the great rate at which it develops even at very low temperatures. The regularity of the rearrangement (reconstruction) of the lattice stipulates a regular orientation of the lattice of the new phase to the original one, and this fact is always observed in this type of transformations.

The strain transformation observed by the authors in copper-zinc alloys belongs evidently to this second type of transformations. We quite agree with the authors that it is necessary to choose a common term for these transformations; moreover, that they occur sufficiently often in alloys, as investigations of recent years have proved.

The term "strain transformation" does not seem to us quite suitable, because transformations of a similar type are observed also where it seems that no strains should arise; viz., in very slow cooling (very slow passing through the transformation point or region). As the forces that cause these transformations are not known, we think that, taking into consideration the history of the development of this problem, it would be more rational at present to give transformations of this type the name of martensite transformations.

The question of martensite transformations in copper-zinc alloys attracted our attention, owing to the observed similarity between diagrams of copper-zinc alloys and one of the diagrams of a metastable state in copper-aluminum alloys.[27,28,29] In much the results of our investigations are similar to the results obtained by Greninger and Mooradian.

The authors point out that they have been unable to confirm the formation of a face-centered tetragonal lattice after quenching similar to the one observed by Kaminsky and Kurdjumow.[28]

It should be noted, however, that the transformation of a beta lattice into a tetragonal alpha prime (Fig. 17*a*) has been observed by us only in alloys containing about 1 per cent of lead and tin, and then only if the quenching process was conducted very intensively.

If the rate of cooling was not high enough, the alpha phase was partly precipitated, and in consequence the beta phase became enriched in zinc. In this case no transformation of the beta lattice into a tetragonal one was observed during the quenching; transformation occurred, as the thermic cooling curves showed, only at temperatures below room temperature. X-ray patterns obtained in a low-temperature camera (liquid air) showed that in this case the lattice differed from a tetragonal alpha prime lattice.[30] The disposition of the lines has much in general with their disposition on

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[28] E. Kaminsky and G. Kurdjumow: *Metallwirtschaft* (1936) **15**, 905.

[29] V. Gawranek, E. Kaminsky and G. Kurdjumow: *Metallwirtschaft* (1936) **15**, 370.

[30] I. Isaitschew and V. Miretsky: X-ray Study of Transformation of *d* Phase in Cu-Zn Alloys at Low Temperatures. Diploma work by Miretzky reported at Kiew University, June, 1936. In press.

X-ray patterns of the beta prime phase of copper-aluminum alloys, but their number is greater in the first case.

In alloys prepared from electrolytic copper and Zink Kahlbaum, the formation of a tetragonal lattice during quenching was not observed, and in this our observations coincide rather well with those of Greninger and Mooradian. Transformation was observed only when the metastable beta phase was cooled to low temperatures. Fig. 18 shows X-ray patterns obtained at 20° and −160° C. of an alloy with 40 per cent zinc and quenched from 860° C. In this also we found a system of lines different from the one of tetragonal lattice alpha prime and similar to the system observed on X-ray patterns of alloys containing impurities and taken at low temperatures. *d* values found by Isaitschew and Miretsky[30] and those found by Greninger and Mooradian (Table 4) agree well, taking into consideration the comparative low accuracy of the reflection angle measurements.

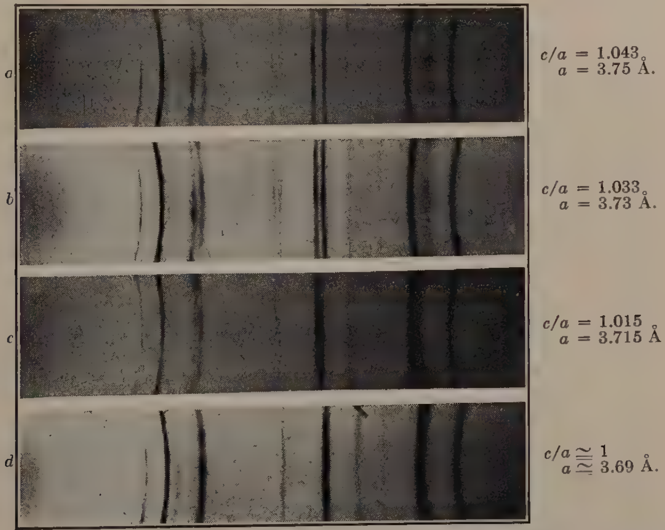

FIG. 17.—COPPER-ZINC ALLOY, 39 PER CENT ZN (ALLOY WITH IMPURITIES). DEBYE PATTERNS AT ROOM TEMPERATURE. FE RADIATION.

a, quenched from 860° in 10 per cent solution of NaOH.
b, tempered 15 min. at 140°.
c, tempered 3 hr. 30 min. at 140°.
d, tempered 24 hr. at 140°.

When the concentration of zinc is increased, the quantity of transformed beta phase diminishes, and at a 42 per cent concentration no transformation of the beta phase was observed under low-temperature conditions (−160°). Available data indicate that the temperature of the beginning of a martensite transformation of the beta phase quickly drops as the concentration of zinc increases (compare temperatures $\beta_1 \rightarrow \beta'$ and $\beta_1 \rightarrow \gamma'$ in alloys of copper-aluminum, temperature Ar″ in steels).

The fact that different lattices are obtained during the process of "diffusionless" transformations depending on the concentration is not new, and a similar phenomenon was observed in copper-aluminum alloys where up to 13 per cent Al there is a $\beta_1 \rightarrow \beta'$ transformation and above 13 per cent Al a $\beta_1 \rightarrow \gamma'$ transformation.[31,32] It is possible that the absence of a tetragonal lattice in pure alloys may be explained by the supposi-

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[31] G. Kurdjumow and T. Stelletzkaja: *Tech. Phys.* U. S. S. R. (1935) **2**, No. 1.

[32] G. Kurdjumow and G. Sachs: *Ztsch. Phys.* (1936) **64**, 325.

tion that at concentrations at which it should appear a greater cooling rate is required, in the absence of impurities, in order to prevent the precipitation of the alpha phase at high temperatures and consequently the enrichment of the beta phase in zinc.

We explain the formation of the tetragonal lattice by an ordered arrangement of the atoms of copper and zinc in a face-centered lattice similar to the arrangement in a copper-gold lattice. We explain the formation of such an ordered lattice by the fact that during the cooling of the alloy the disordered beta phase at first changes into an ordered beta phase with a Cs-Cl lattice, which during further cooling undergoes the martensite transformation.

As we consider that during this process the atoms do not interchange places, but only shift relatively to one another, the arrangement in the new lattice must be an ordered one. In fact, if we apply the mechanism of lattice reconstruction proposed by one of us together with Sachs,[32] the reconstruction results in an arrangement of the atoms[28] similar to their arrangement in copper-gold.

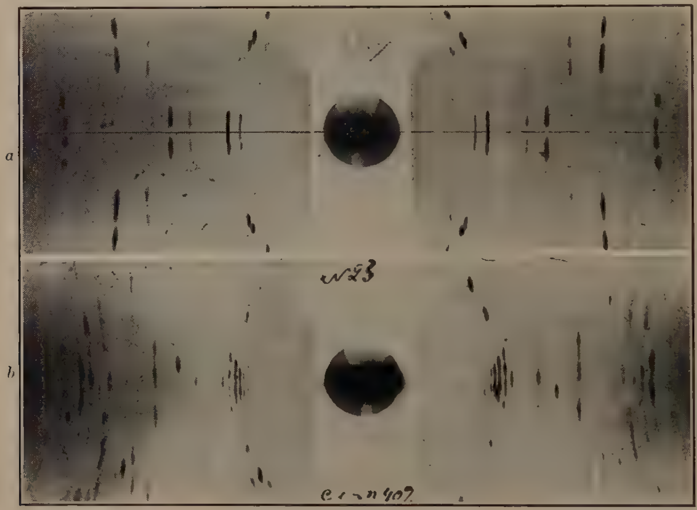

FIG. 18.—COPPER-ZINC ALLOY, 40 PER CENT Zn (PURE ALLOY) QUENCHED FROM 860°. ROTATION OF CRYSTAL PATTERNS, Co RADIATION
a, at room temperature; *b*, at −160° C.

When the alpha prime phase is heated to a temperature of 125° to 200° C., a disordering process takes place. At a temperature of 125° this process still develops very slowly, but at 170° to 200° it ends in a few minutes.

The distance between the doublet lines of the tetragonal lattice gradually diminishes (Fig. 17) and lattice alpha prime turns by degrees into lattice alpha.

The tetragonal lattice forms only in alloys that are very close to the alpha-phase boundary, and it is possible only in that region of concentrations where the alpha phase and not alpha plus beta is stable at room temperature.

We have not been able to define yet the structure of the lattice that forms at low temperatures, although the resemblance of the X-ray pattern of this phase to the X-ray pattern of the beta prime phase of copper-aluminum alloys permits us to presume that it represents a slightly deformed hexagonal close-packed lattice. Lately the martensite phases beta prime and gamma prime of copper-aluminum alloys, which for a long time remained undefined, have been determined in our laboratory. The gamma prime phase has a hexagonal close-packed lattice with an ordered arrangement of atoms;

beta prime lattice differs from the alpha prime in that the [001] direction deviates from the normal to plane (001) at an angle of about 2°, and the angle between the planes (100) and (010) differs about 1° from 120°. The beta prime and gamma prime lattices check very well with the Debye X-ray patterns as well as with the pole figures constructed for most planes.

The X-ray patterns of copper-zinc alloys have however a greater number of lines than the patterns of the beta prime lattice of copper-aluminum alloys. It may be possible that here there are two different lattices, as in copper-aluminum alloys, where at a concentration from 12.9 to 13.2 lattices beta prime and gamma prime occur simultaneously.[31]

A very interesting fact observed during the study of the beta-phase transformations in copper-zinc alloys consists in the reversibility of the martensite transformation as concerns the lattices and their orientation. A monocrystal sample was repeatedly cooled from room temperature to the temperature of liquid air, and each time the X-ray patterns showed a regular orientation of the new phase and the original orientation of the beta crystal. From this it follows that the lattice reconstruction (atom shifting) during a transformation from the martensite phase into the beta phase proceeds along the same lines as during the formation of a martensite lattice, only in an opposite direction.

The perfect reversibility of the martensite transformation up to the present time was observed unquestionably only in this case and in the case of transformations of $\beta_1 \rightarrow \beta'$ of copper-aluminum alloys. The reversibility of martensite transformations permits us to make a number of conclusions concerning their nature, but we are unable to speak about them here in detail. The study of martensite transformations in copper-zinc alloys represents a special interest, as in these the process develops in its pure form, being free from the processes of the first type (diffusion processes, growth of crystals).

During the cooling of alloys containing 25.69 per cent Sn, the authors observed no transformation. Apparently, the concentration of tin in this alloy is sufficiently high and the transformation takes place at a temperature below the temperature of liquid air. During the study of transformations in copper-tin alloys, Isaitschew observed martensite transformation at low temperatures in alloys with a lower concentration of tin. In Fig. 19 are shown the X-ray patterns (room temperature) of quenched alloy containing 25 per cent Sn after its immersion into liquid air. On this figure can be seen, in addition to beta-phase lines, a new system of lines.

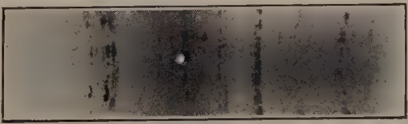

Fig. 19.—Copper-tin alloy, 25% Sn. Debye patterns obtained at room temperature after quenching and immersion in liquid air. Fe radiation.

Very interesting experiments were made by Greninger and Mooradian during their study of the transformation of metastable beta phase directly under room temperature, using a microscope. Their results confirm clearly the statement that this transformation belongs to transformations of the martensite type. Instantaneous appearance of markings with the decrease of temperature, the ceasing of transformation if the specimen is maintained at a constant low temperature, absence of a definite critical temperature and the presence of a temperature region in which transformation occurs, all these phenomena are characteristic of martensite transformations and were observed during austenite-martensite transformation in steels. But a new phenomenon—the disappearance of markings with the rise of temperature—has been observed by the authors. This is in complete agreement with the authors' and our X-ray data and with our results of thermal analysis, which show that the martensite transformation of the metastable beta phase is reversible. It would be interesting to know whether the disappearance of the individual markings is also instantaneous. Kinetic of reverse martensite transformation $\beta' \rightarrow \beta_1$ in copper-aluminum alloys was studied by Gridnew[33] by means of the microcinematographic method nearly in the same way as it was carried out for austenite-martensite transformation by Wister.[34] The quenched alloy containing a beta prime phase was polished and then heated. The change in volume led to the formation of a relief on the polished surface and made it possible to observe the transformation under a microscope or on a cinema film. After the transformation $\beta' \rightarrow \beta_1$, a needle structure appeared on the surface of the specimen. The cinematographic examination showed that individual "needles" of the β_1 phase form in less than 0.1 sec. Gridnew also observed sometimes the "growth" of the needle of β_1 phase. But this growth is not continuous and occurs by "instantaneous increments," as the "growth of markings" observed by Greninger and Mooradian.

TABLE 4.—*d Values Taken from X-ray Patterns Obtained at Low Temperatures*

Obtained by Greninger and Mooradian	Obtained by Isaitschew and Miretsky	Obtained by Greninger and Mooradian	Obtained by Isaitschew and Miretsky
	2.26	1.18	
	2.19	1.145	1.145
?	2.13	1.132	1.138
	2.04		1.118
1.96	1.96	1.095	1.092
1.87	1.88	1.068	
	1.61		1.027
1.33	1.33	0.872	
1.29	1.295	0.859	
1.24	1.235	0.853	
		0.835	

Interesting results were obtained by the authors concerning transformations arising during the deformation of the metastable beta phase. Here the X-ray patterns are nearly the same as patterns taken at low temperatures, but not all the lines coincide; besides, changes in the line system were observed as the degree of deformation increased. The deformation should rise with the temperature of martensite transformation, as it has been found for steel. Therefore the transformations during deformation (at room temperature) and during cooling to low temperature may be of the same nature. But deformation may bring about further changes in the new metastable "martensite lattice." Increase of the deformation degree causes, as the authors point out, the broadening, shifting or merging of some lines. The change of the lattice of the martensite phase was observed by one of us with Stelletzkaja while studying the influence of deformation on the beta prime phase of copper-aluminum alloys and its decomposition on tempering. After deformation some lines on Debye patterns of the beta prime phase merged together, giving broad lines; the new line system becomes analogic to the line system of gamma prime phase, which has a close-packed hexagonal lattice. As pointed out above, the beta prime phase has a little deformed hexagonal close-packed lattice. It may be concluded therefore that the mechanical treatment leads in this case to the shifting of atoms in the direction of formation of a more close-packed structure.

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[33] V. Gridnew: *Phys. Ztsch.* U. S. S. R. In press.

[34] H. Wister: *Ztsch. Metallkunde* (1932) **24**, 276.

The changing of crystal structure of metastable phases during deformation is of great importance in understanding phase transformations and it is desirable to further study this question.

A. B. Greninger (written discussion).—It is gratifying to find that the results of Isaitschew, Kaminsky and Kurdjumow's work on the martensite transformation in beta brass agree so well with our own, and that the previous discrepancy is explained by the fact that the tetragonal alpha prime lattice was obtained on quenching only in alloys containing about 1 per cent of lead and tin. The assumption that the alpha prime lattice resembles the copper-gold structure is well substantiated by the data contained in Fig. 17, for the decomposition of alpha prime copper-zinc on tempering appears to be similar to the disordering process that occurs on tempering the ordered copper-gold alloy, and superficially at least, quite different from the decomposition of martensite in steel. It would appear desirable to test the alpha prime structure for the presence or absence of order, using zinc characteristic X radiation—a method that has proved successful in establishing the presence of order in stable beta brass.[35]

The remarks of Isaitschew, Kaminsky and Kurdjumow on the $\beta_1 \leftrightarrows \beta'$ copper-aluminum transformation are of particular interest to me, for I have also been studying this transformation. Representing as it does the most easily controlled martensite process of the reversible type, it is only natural that this transformation should receive much attention. The results of Gridnew's microscopic work, referred to by the writers, are interesting and agree with the recent work of Obinata,[36] who also has made a cinematographic study of the $\beta_1 \leftrightarrows \beta'$ copper-aluminum transformation. A complete solution of the crystal structure of beta prime copper-aluminum (or of the equivalent structure in copper-zinc alloys) would represent, I believe, the most important single contribution that could be made to our knowledge of lattice transformations. Dr. Samans is indeed correct in his evaluation of the importance of this "missing link." I have already succeeded in obtaining a partial solution to the structure of beta prime copper-aluminum and am confident that a complete solution is possible. The data I have obtained so far do not agree with the brief description of the cell given by Isaitschew, Kaminsky and Kurdjumow; however, it will be best to await the publication of both complete solutions before a detailed comparison is attempted.

Isaitschew has remarked on the fact that the Debye patterns of beta prime copper-aluminum and the equivalent copper-zinc structure are markedly different; and although it may be that in the latter there are two lattices instead of one, I prefer to attribute the difference to superlattices and the role they may have in the martensite transformation. Thus, if the beta lattice becomes ordered in copper-zinc (as we know it does in Cu_3Al)[37] just before the martensite transformation, we would not expect the two martensite lattices (or their habits) to be identical, inasmuch as the two lattices that are transforming would not be the same. I feel that martensite processes are in some way intimately connected with order—disorder transformations —and that this factor should be considered not only when we attempt to correlate the behavior of one obviously martensitic process with another but also in correlations between martensite transformations and other transformations whose "martensitic characteristics" are not so clearly or easily revealed as those in the three alloys mentioned above.

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[35] F. W. Jones and C. Sykes: The Superlattice in β-Brass. *Proc.* Roy. Soc. (1937), **161,** 440.

[36] I. Obinata and M. Hayashi: On the Nature of the Transformation in Aluminum Bronze, V—Change in Structure Due to the Transformation. *Jnl.* Iron and Steel. Inst. Japan (1937) **23,** 1092–1099.

[37] G. Wassermann: Über die Umwandlungsvorgänge in β-Aluminiumbronze. *Metallwirtschaft* (1934) **8,** 133–139.

Dr. Samans' carefully developed analysis constitutes a welcome addition to our paper. Analyses of this sort are apt to prove helpful in the study of martensite processes so long as we recognize that the movements proposed represent at best a vector breakdown of the unknown real path of the transformation. Also, it is necessary in dealing with such highly speculative subjects clearly to separate theory from fact, something that Dr. Samans has neglected to do in his statement: " . . . the plane and direction of shear for this first step are identical with those found by Mathewson and Edmunds for twinning in body-centered cubic metals. . . . "

Judging from the general tone of the discussions, one need no longer hesitate to use the term "martensite" to designate alloy transformations that are analogous to the martensite transformation in steel. It will, of course, be recognized that it will not always be possible to classify a given alloy transformation as martensitic or nonmartensitic, for the martensite transformation, as a physical process, is not yet amenable to precise definition, such as can be given, for example, to the order-disorder transformation. We must rely on criteria that are truly empirical, obtainable only under experimental conditions that make it difficult or impossible to separate the important from the unimportant, or to distinguish cause from effect. For example, the structure referred to by Dr. Smith in his discussion is face-centered cubic when prepared in alloys of high purity, yet when certain impurities are present the alloy is face-centered tetragonal after severe quenching. (See discussion by Isaitschew, Kaminsky and Kurdjumow.) This structure is but one of many that result from transformations that apparently proceed by the martensite process, yet have crystal structures of the equilibrium phases.

A most necessary requirement for advance in this field is a more general recognition among metallurgists of the several ways in which martensite transformations may be manifested. Many valuable data undoubtedly have been lost to the literature through failure to consider the martensite reaction in the interpretation of "unusual" experimental results. It is encouraging to have two current examples of research problems mentioned in the discussion (one by Dr. Ageew and one by Dr. Swartz) in which considerations of martensite reactions have been of assistance.

Deformation of Beta Brass

By Alden B. Greninger,* Junior Member A.I.M.E.

(New York Meeting, February, 1938)

In a recent study[1] of the deformation of metastable beta copper-zinc and beta copper-tin crystals, it was established that the parallel markings that appear on the surface of these crystals after slight deformation represent lattice transformations. Stereographic analysis showed that in beta copper-tin, the poles of these markings deviated one or two degrees from poles of the form {133}. In beta copper-zinc the plane delineated by the markings corresponded to no one crystallographic plane of the matrix lattice; the marking poles deviated from 5° to 11° from poles of the form {110}, and were displaced only a few degrees from ⟨110⟩ zones. Inasmuch as the new transition lattices produced as the result of the deformation are different for each alloy, it was thought at first that the habits of the markings might be the result of a cooperation between matrix lattice and transformed lattice. (Both matrix lattices are body-centered cubic.) Such a cooperative effect is thought to obtain in the formation of Widmanstätten figures, for it is well known that the matrix lattice alone does not determine the habit assumed by a segregate phase. On the other hand, it is not inconceivable that the dissimilarity in marking habit might be due to differences in deformation characteristics of beta brass and beta bronze. Barrett and co-workers[2] have shown that slip-line habits in pure iron are markedly different from those in high-silicon ferrite; and although it has been repeatedly demonstrated that plates of a segregate phase do not necessarily form on the slip planes of the matrix lattice, deformation characteristics may be more intimately allied with plate formation when a transformation is made to occur as a result of plastic deformation. However, there is the fact that the orientation of markings in metastable beta copper-zinc is the same whether the markings be produced by quenching, deformation, or liquid-air cooling; likewise, quenching and deformation markings in metastable beta copper-tin are oriented in the same way with respect to the beta matrix.

During the course of the investigation referred to above, samples of 52:48 (stable beta) copper-zinc† were deformed and examined micro-

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Manuscript received at the office of the Institute Nov. 12, 1937.

* Instructor in Metallurgy, Graduate School of Engineering, Harvard University Cambridge, Mass.

[1] References are at the end of the paper.

† Beta copper-tin is stable only at high temperatures.

scopically. The preliminary observations warranted a more thorough study of the mode of deformation of beta brass, particularly so in view of the present uncertainty as to the identity of the plane of slip in this crystal, coupled with the fact that the marking planes in metastable beta brass are only a very few degrees removed from the plane of greatest atomic density in the body-centered cubic lattice.

Previous Work

In sharp contrast to the behavior of face-centered cubic metal and alloy crystals, in which the slip plane is consistently the octahedral $\{111\}$, body-centered cubic crystals evidently possess a variety of slip planes.* Thus, according to Barrett, Ansel and Mehl,[2] pure iron slips on $\{110\}$, $\{112\}$ and $\{123\}$, while in high-silicon ferrite slip is on $\{110\}$ only. Goucher[3,4] states that tungsten slips on $\{112\}$ in a $[111]$ direction; however, the data advanced in support of this statement cannot be considered conclusive. Von Göler and Sachs[5] early reported the observation† of slip bands on a single-crystal rod of beta brass; the bands coincided within the limits of error (3°) with traces of a $\{110\}$ plane. Taylor,[6] however, observed no slip bands in his experiments on the deformation of single crystals of beta brass; he concluded from distortion measurements that the "active slip plane" was located between $\{110\}$ and $\{112\}$ and that the direction of slip was $[111]$. Taylor further demonstrated experimentally that for all possible planes through the direction of slip $[11\bar{1}]$, the resistance to shear was at a minimum when the distortion plane coincided with a plane of the type $\{110\}$, and a maximum resistance to shear was encountered when the deformation plane was in the neighborhood of $\{112\}$. The most recent work is that of Elam,[7] who emphasized the fact that slip bands are observed in beta brass (after deformation) only when the preceding polishing operation is carried out with considerable care. Elam concluded that there was no essential difference in the behavior of beta-brass and iron crystals distorted in tension. She stated that slip bands usually corresponded with either $\{110\}$ traces or, less frequently, with $\{112\}$; however, distortion calculations showed that slip did not continue on these planes throughout the extension, and that the direction of slip was not always $[111]$. She concluded that distortion did not proceed by slip on a definite crystallographic plane. Unfortunately, Elam made no mention of the order of accuracy of measurements; she merely states: " . . . allowing for errors in measurement, the deviation of the actual slip band from traces of crystal planes is still often large." Elam noticed an additional laminated surface feature (resulting from deformation) on beta-brass crystals, making small angles with, and apparently distinct from, slip bands. These she described as "broad bands" and stated that they did not always agree with any likely crystal plane; the suggestion was made that these broad bands and possibly the distortion planes correspond to Lüder's lines.

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* The early work on the deformation of body-centered cubic crystals, especially iron, has been summarized recently by Barrett, Ansel, and Mehl.[2]

† This observation was incidental to their study of the $\beta \leftrightarrows \beta'$ transformation in brass.

MATERIALS AND METHODS

The alloy used in the present investigation was supplied by Dr. Cyril Stanley Smith, of the American Brass Co., in the form of rolled plates. The analysis was: copper, 51.89 per cent; zinc, 48.10; lead, 0.001; iron, 0.011; cadmium, 0.002. Rectangular specimens approximately ½ by ½ by ⅜ in. cut from the plates were rough-ground, heat-treated, and then polished on two or three surfaces. Specimens were studied in the solidified, in the annealed (β'), and in the quenched (β) conditions. For the annealing and quenching operations the temperature employed was 855° C., and a time-at-temperature of about five minutes was found to be sufficient to produce grains ranging in size from 2 to 6 mm. To prepare the as-solidified specimens, a rectangular specimen, described above, was packed in powdered graphite, heated to about 950° C., and cooled at such a rate that the grain size was roughly the same as that in the recrystallized specimens. Specimens were very lightly deformed by hammering or by squeezing in a vise; surface characteristics were then studied and measured microscopically. The specimen was then etched deeply in dilute HNO_3 and the orientations of the pertinent grains were determined by means of the back-reflection Laue X-ray method.[9] Trace normals and crystal poles were plotted stereographically. The over-all inaccuracy in the location of traces with respect to crystal poles is estimated at $\pm 1°$; a few determinations are undoubtedly more accurate than this. In general, it was possible to locate only trace normals, not poles, of slip planes; that is, the bands were not sufficiently prominent to permit a direct visual matching of a set on one surface with a set on another. However, a few poles were located indirectly in a few cases where for a distance of a millimeter or so along the edge only one set of bands was present on each of the two surfaces and each set continued to the edge.

RESULTS

Two apparently distinct structural characteristics appear on a polished surface of 52:48 (beta) copper-zinc after slight deformation: (1) sets of parallel fine hairlike lines, undoubtedly slip bands, and (2) a corrugated relief which under oblique illumination imparts a coarse light-and-dark banding effect to the surface of a grain (see Figs. 3 to 6). The latter will be referred to as "deformation bands." Neither slip lines nor deformation bands continue over a grain boundary without changing direction; hence, both must be related in some way to the beta lattice. Prominent deformation bands are easily visible with the naked eye; under the microscope they are generally discernible only with oblique illumination. Likewise, slip lines are difficult, in many cases impossible, to see with vertical illumination. Slip lines in beta brass are decidedly less prominent than those in face-centered cubic metal and alloy crystals.

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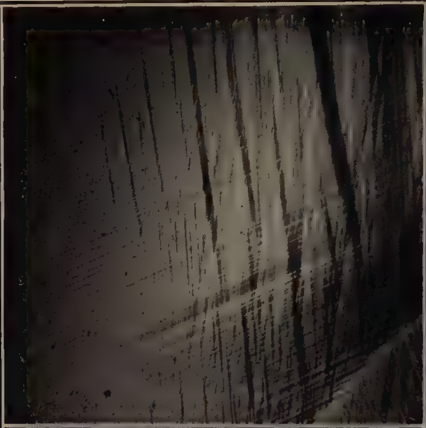

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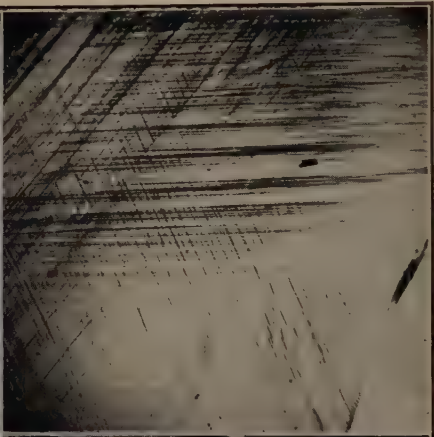

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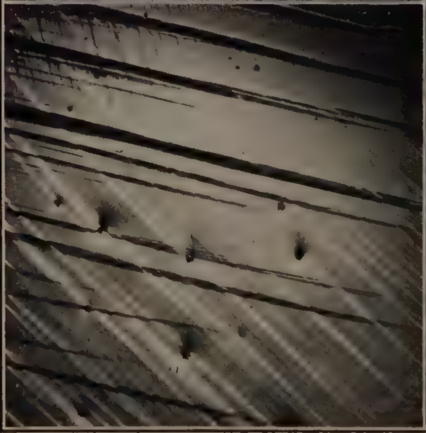

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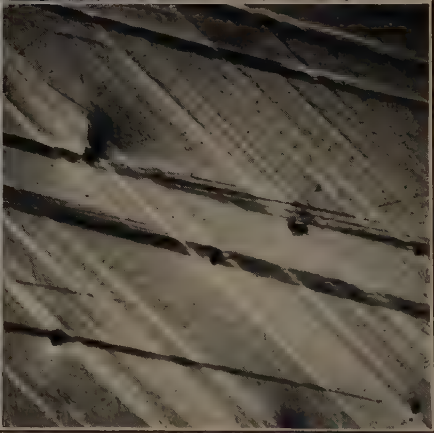

Fig. 1.—Beta brass, quenched from 855° C., polished and deformed; unetched; oblique illumination. × 50.

The fine white lines are typical of well defined slip lines in beta brass. The vertical set (dark) contains both slip lines (fine) and deformation bands (broad).

Fig. 2.—Beta brass, quenched from 855° C., polished and deformed; unetched; oblique illumination. × 40. Shows slip lines.

Fig. 3.—Deformation bands in deformed (as solidified) beta brass; unetched; oblique illumination. × 40.

Fig. 4.—Same as Fig. 3, but × 80.

Shows slip lines as a component part of the broader deformation bands. The fine component lines were found to deviate ½° from {110} traces; the broad bands are inclined at about 4° to {110}.

The behavior of beta brass, in so far as the production of slip lines and deformation bands is concerned, appears to be about the same under both static and dynamic deformation. However, deformation bands are somewhat more prominent than slip lines in specimens deformed in the as-solidified condition, whereas the reverse is true for specimens in the recrystallized (annealed or quenched) condition. Specimens containing many grains display slip lines of greater regularity than those of only a few grains. A recrystallized specimen will after slight deformation normally show one or more sets of slip lines in every grain. Individual members of a set of well defined slip lines are normally parallel to within ±0.5°, while deformation bands vary considerably in their regularity. Orientation studies were confined to lines and bands which could be measured accurately; no attempts were made to measure irregular bandings of the type shown in Fig. 7.

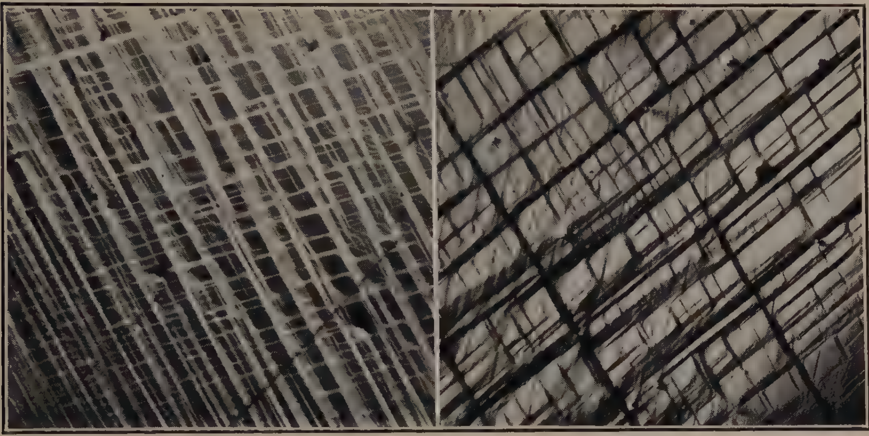

Fig. 5. Fig. 6.

Figs. 5 and 6.—Deformation bands in deformed (as solidified) beta brass; unetched; oblique illumination. × 40.

Both sets of broad bands deviate about 4° from {110} traces. The two widely separated dark lines in Fig. 5 deviated 1½° from a {110} trace.

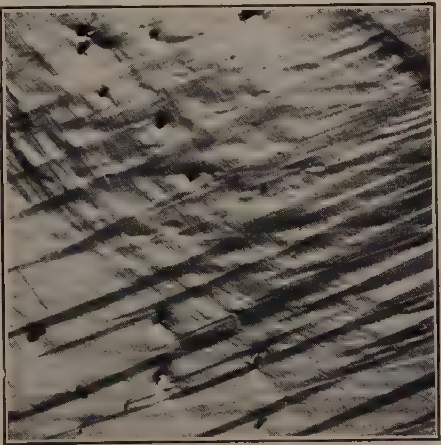

Fig. 7.—Irregular bandings in deformed (as solidified) beta brass; unetched; oblique illumination. × 40.

This irregular type of surface upheaval is not uncommon.

A summary of orientation results is given in Table 1. The data indicate clearly that slip in beta brass is on {110}; the broad bands measured deviate 2° to 7° from {110}. From the microscopic examination of these and many additional specimens, it was observed that in grains containing a prominent set of broad bands slip lines are present as an apparent fine structure of the broad bands and are inclined at an angle of a few degrees to their general direction (Fig. 4). As a rule, broad bands can be differentiated easily from slip lines; that is, if microscopic examination should reveal sharp parallel lines such as are shown in Fig. 1, it may be predicted with assurance that the lines are slip lines, and, furthermore, that they are accurately parallel to $\{110\}$. Likewise, slip lines and broad bands may be identified easily when they occur together (i.e., superimposed), as in Fig. 4, and thus their orientations may safely be predicted. Occasionally, however, it is not possible to make a positive identification; in other words, deformation bands are not always broad (for example, see Fig. 6), nor are slip lines always well defined. To this latter classification belong two of the "slip lines" in specimen II, which showed a deviation of 4° and 6°, respectively, from $\{110\}$.

TABLE 1.—*Deviations of Slip Lines and Deformation Bands from* $\{110\}_\beta$
DEGREES

Specimen No.	Grain	Condition	Apparent Slip Lines		Apparent Deformation Bands	
			Trace Normals	Poles	Trace Normals[a]	Poles
1	A	As solidified	1			
	B			1		6
2	A	Quenched	4, ½, 3½		6	
	B		1, 3, 6			
3	A	As solidified	½, 1			
	B		1, ½		5	
	C		1, 1½, 0		4½, 7	
4	A	Furnace-cooled	½, 1, 1½			
	B		1, 1, 0			
5	A	Quenched	1½, 2½, 1½			
	B		½	1½, 2, 3½		
	C		0, 2½	1		
	D		1	1		
	E		0, 1, 1			
	F		1, 1, ½			
6	A	Quenched	2, 0			
	B		½, ½			
	C		0			
	D		½, 0			
7	B	Quenched	0, 1			
8	A	Quenched	1, 2			
	B		0, 3			
9	A	As solidified	0, ½, 1		5, 4, 2, 2	
	B		1½		4, 4	

[a] Measured where possible to the point at which the trace normal passes through the $\langle 110 \rangle$ zone.

Neither slip lines nor deformation bands are revealed after repolishing* and etching with the usual $NH_4OH + H_2O_2$ etching reagent. However, vestiges of these bandings are often revealed after deep etching with dilute HNO_3. That the production of deformation bands does not involve any considerable change in orientation (such, for example, as would be produced by a twinning movement) is evidenced by the fact that when slip lines pass through deformation bands they do so with little or no change in direction. Optical examinations of etch-pit reflections from specimens etched, after deforming, in $HNO_3 + Ag$, occasionally revealed slight orientation differences in regions formerly occupied by deformation bands; however, these differences in orientation were too small to measure. Back-reflection Laue patterns taken on heavily banded areas of a grain (like that shown in Fig. 6) after light etching showed nothing more unusual than a considerable broadening of the Laue spots.

Thus, it would appear that the lattice movement involved in the production of deformation bands is not greatly different from that which produces slip lines. The composite effect shown in Fig. 4 is sufficiently common to be called a general characteristic of deformation bands, and it may well be that these bands represent nothing more than a composite slip movement having directional components that differ from those of "pure slip." If the directional components differ throughout the body of the grain as well as on the surface (and there is no reason to believe they do not), this would mean that although unit slip in beta brass is on $\{110\}$, the effective plane of slip or distortion would be inclined at an angle of some few degrees to the unit slip plane. Slip of this type would probably call for considerably more "lattice rotation" than would the more conventional type.

Whatever may be the exact relationship (in terms of lattice movement) between slip lines and deformation bands, there can be no doubt that this tendency for bandings to be slightly displaced from $\{110\}$ is a definite characteristic of the deformation of beta brass. It should be noted that broad deformation bands (but not slip lines) may be produced in metastable beta brass,[1] and that transformation markings in this alloy, whether produced by quenching, deformation, or liquid-air cooling, are likewise inclined at angles of a few degrees to $\{110\}$.

CONCLUSIONS

1. Polished specimens of beta brass subjected to light deformation show: (1) slip lines, and (2) deformation bands. The latter appear to represent a composite slip movement having directional components

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* In order that this statement be strictly true, the repolishing operation must be prolonged sufficiently to erase all evidence of surface relief.

differing from those of pure slip. Slip in beta brass is on {110}; the broad corrugations are inclined at angles of a few degrees to {110}.

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DISCUSSION

(*Jerome Strauss presiding*)

C. S. Barrett,* Pittsburgh, Pa. (written discussion).—I have made some qualitative determinations of the slip mechanism in tantalum, which is also body-centered cubic, that might be of interest. Slip lines in tantalum tend to be wavy and resemble very closely those of alpha iron, thus suggesting that the alpha-iron slip mechanism operates in tantalum rather than the {110} mechanism of beta brass and high-silicon ferrite, which produces straight lines in parallel sets or in angular patterns. My observations happened to be made on some crystals that had been reduced 15 per cent by cold-rolling previous to the metallographic polishing, but back-reflection Laue patterns of the crystals were reasonably free from distortion, and it seems very unlikely this prior deformation altered the mechanism appreciably.

Banding of the type observed in beta brass is not common in other body-centered cubic metals. Using low degrees of deformation, I have failed to see any evidence of it in iron, in tungsten, or in tantalum. Pfeil has reported banding in iron crystals that have been severely compressed, but he observed it after etching, so his bands are probably not analogous to those in beta brass. The observations that the relative prominence of the bands compared with the lines is a function of both the alloy composition and the thermal history of the sample suggests that the conditions responsible for the banding may be related to: (1) the degree of order in the superlattice or (2) the presence of "soft spots" or voids in the crystal—some sort of regions, of dimensions comparable to the width of the deformation bands, where slip starts easily on several adjacent crystallographic planes. I wonder whether the author would give his opinion as to whether or not the bands are merely close-packed parallel groups of ordinary {110} slip lines.

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* Metals Research Laboratory, Carnegie Institute of Technology.

C. H. Samans,* State College, Pa. (written discussion).—In connection with some work that was done with cold-rolled single crystals of alpha brass at the Hammond Laboratory a few years ago, we encountered practically the same thing that Dr. Greninger has reported here for beta brass. We were working with a 70:30 alloy and naturally the surfaces that were in contact with the rolls were nicely smoothed, but the sides of the specimens were irregular and under oblique illumination showed bandings of very nearly the same kind as those found by Dr. Greninger. Inasmuch as the deformations involved were much heavier, the bands were more apt to be irregular, but we noticed the same slight deviation of the broad markings from the fine slip lines even though no measurements of these deviations were made. This suggests to us two possible explanations for his markings. In the first place they could be caused by the same phenomenon to which we attributed ours; namely, "a layerlike" deformation of the grain, a different slip system acting in alternate layers and each layer, consequently, deforming differently with respect to the original surface. This would produce ridges and valleys in the surface, which, under oblique illumination, would appear as broad markings containing fine slip bands. In the second place, the restraining influence of the surrounding grains in his polycrystalline aggregate could produce effects comparable to those imposed by the roll surfaces upon our specimens. As a result the surface of his specimens might deform by bulging or a similar effect simply because it could not deform in any other way. Of the two possible explanations, I am inclined to favor the former, though, as he has presented no information relating the markings to the orientation of the original beta grain, it is impossible to check this relationship.

Our only other comment on the paper relates to the question of choice of terminology, and as we realize his difficulties in this respect it must not be considered as particularly serious. In the field of alpha brass we have rather usurped the terms "deformation bands" and "deformation markings" to designate markings produced by mechanical strain that are not eliminated by repolishing. I believe them to be mechanical twins, though there still seems to be some disagreement on that point. With this in mind it seems rather unfortunate that he should have chosen these terms to describe his bandings, because they are eliminated by repolishing and in the minds of persons who are not particularly familiar with his work this is likely to introduce a confusion and a misunderstanding, both of which we should endeavor to avoid if possible in our metallurgical literature.

A. B. Greninger (written discussion).—In answer to the question raised by Dr. Barrett: I feel that the deformation bands in beta brass represent something more than merely close-packed parallel groups of {110} slip lines. There is a pronounced similarity between the microstructures of deformation bands in stable beta brass and the strain transformation markings in metastable beta brass. This fact has been commented upon by Dr. Derge (see p. 356); however, it is not at all clear just how these two structures may be related.

It is interesting to find that Dr. Samans has observed similar structures in alpha brass, although additional data would be needed before the similarity or identity could be considered as an established fact.

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* Assistant Professor of Metallurgy, School of Mineral Industries, The Pennsylvania State College.

Effect of Chromium on the Grain Growth of Brass

By B. W. Gonser,* Member A.I.M.E., and C. M. Heath*

(Atlantic City Meeting, October, 1937)

The importance of grain size and its control in wrought brass needs no lengthy discussion, since specifications so often make exact control imperative. Aids to this control are therefore of interest.

The effect of a number of different elements on the grain growth of brass under various conditions of annealing has been reported in the technical literature. In particular, a paper by Cook and Miller[1] a few years ago, with the discussion that followed, gave valuable information on the effects of iron, phosphorus, manganese, aluminum, aluminum plus nickel, and aluminum plus silicon. Price,[2] in his discussion of that paper, added a description of some commercial brasses that exhibited a grain-refining effect owing to the presence of 2 per cent Al and 1 per cent Ni. Gibson and Doss[3] have recently given data on the effect of iron on annealing high brass. No comprehensive study, however, has been given to the effect of additions of chromium.

It has been the purpose of this investigation to determine the effect of adding various amounts of chromium to a plain cartridge brass, particularly in regard to the effect on grain growth in various annealing treatments after cold-working.

Preparation of Alloys

Alloys of high-purity brass of 68.5 Cu, 31.5 Zn composition were made containing from 0 to 0.17 per cent Cr. These were produced in induction furnaces, using unlined graphite crucibles to hold the charge. The melts were cast into rectangular chill molds giving ingots about ⅞ by 3 by 10 in. in size.

Research conducted at Battelle Memorial Institute for the Union Carbide and Carbon Corporation. Manuscript received at the office of the Institute Aug. 20, 1937.

* Metallurgist and Assistant Metallurgist, respectively, Battelle Memorial Institute, Columbus, Ohio.

[1] M. Cook and H. J. Miller: Effect of Different Elements on Annealing and Grain Growth Characteristics of Alpha Brass. *Jnl.* Inst. Metals (1932) **49,** 247–261.

[2] W. B. Price: *Jnl.* Inst. Metals (1933) **52,** 247–249.

[3] W. A. Gibson and J. H. Doss: Effect of Iron Impurities on the Annealing of High Brass. Amer. Soc. Test. Mat. (1936) **36,** pt. 2, 201–206.

In order to obtain accurately the desired chromium content in the brass under small-scale laboratory conditions, melts of chromium and copper, containing about 0.6 per cent Cr, were first made and portions of these later melted with additions of zinc and more copper to give the final composition desired. Electrolytic zinc and copper were used throughout.

As sources of chromium, both electrolytic chromium and a master alloy containing 90 per cent Cu and 10 Cr, furnished by the Union Carbide and Carbon Research Laboratories, were tried. There was no noticeable difference in the behavior of the final products made from these alloys and as the 10 per cent Cr alloy was far easier to use in making the melts, it was preferred. A recovery of 84 per cent of the chromium added as the 10 per cent Cr alloy was made in the first series of melts compared with only about 40 per cent recovery by adding electrolytic chromium direct. Average recovery of chromium in remelting and diluting to final composition was 90.8 per cent. Analyses of the master alloys and final brass castings are given in Table 1.

For comparison with the effect of chromium, a number of alloys of 68.5 Cu, 31.5 Zn containing up to 0.15 per cent Fe were similarly prepared.

TABLE 1.—*Composition of Alloys*

	Source of Chromium	Composition, Per Cent			
		Cr	Fe	Cu	Zn
Electrolytic chromium....		99.38	0.006		
90 Cu, 10 Cr alloy.......		9.39	0.29		
Intermediate alloy.......	Electrolytic Cr	0.63	0.0056		
Intermediate alloy.......	90 Cu, 10 Cr alloy	0.64	0.020		
Brass alloys:	(Cr free)		0.003	68.6	Balance
113..................	Electrolytic Cr	0.051			
114..................	Electrolytic Cr	0.072			
115..................	Electrolytic Cr	0.093			
116..................	Electrolytic Cr	0.174	0.004	68.97	Balance
109..................	90 Cu, 10 Cr alloy	0.065			
110..................	90 Cu, 10 Cr alloy	0.072			
119..................	90 Cu, 10 Cr alloy	0.107			
111..................	90 Cu, 10 Cr alloy	0.121			
112..................	90 Cu, 10 Cr alloy	0.171	0.008	68.32	Balance

PRODUCTION AND ANNEALING OF BRASS SHEET

As a prerequisite for actual testing, the brass ingots were scalped free of surface imperfections and cold-rolled to thin sheet in such manner that several different degrees of work hardening were obtained. This preparatory treatment consisted of an initial cold reduction of 50 per cent followed by a homogenizing anneal at 750° C., then cold-rolling down to sheet with alternate reductions of about 50 per cent and anneals at 650° C. Thickness of the sheet was so adjusted that final cold-rolling to 0.040 in. thick gave tempers of quarter hard, half hard, hard, and extra hard, or thickness reductions of 11, 20.5, 37 and 50 per cent, respectively.

Annealing and Grain Growth Characteristics

To observe the effect of chromium on grain growth, tensile specimens of the brass sheet that had been cold-rolled to various degrees of hardness were wrapped in copper foil and annealed for ½ hr. at the desired temperature. The resultant grain sizes for the extra hard-rolled brass are shown in Fig. 1. For comparison, the grain size is also shown of samples similarly prepared but using iron instead of chromium.

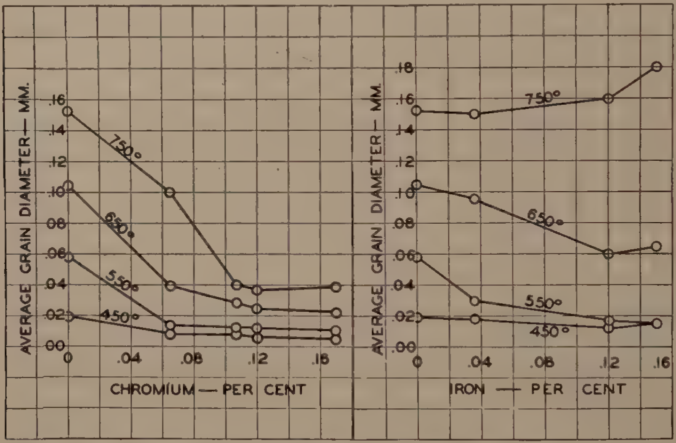

Fig. 1.—Effect of chromium and of iron on the grain size of 68.5:31.5 brass cold-rolled to 50 per cent reduction and annealed for one-half hour at various temperatures.

The very drastic effect of small additions of chromium in restraining grain growth even at high annealing temperatures is unmistakable. Small amounts of iron also decrease the grain size at the lower annealing temperatures, although not nearly as much as corresponding amounts of chromium. Above 700° the restraining influence of small amounts of iron was entirely ineffective.

About 0.10 per cent Cr appears to be the optimum practical amount to be added to 70:30 brass to obtain excellent grain size control for high-temperature annealing. As the annealing temperature is decreased, less chromium is needed to prevent grain growth. Below 600° C., only 0.05 or 0.06 per cent Cr would be needed to produce a satisfactorily small grain. Larger amounts of chromium may decrease the grain size somewhat further, but this advantage may not compensate for changes in the other physical properties. Relatively large amounts of chromium, such as 0.4 or 0.5 per cent, used in preliminary tests, give a very fine grain but the structure is not always uniform and local growth may occur, owing presumably to uneven distribution of the chromium content.

Since iron is an impurity frequently encountered in brass, some work was done on the effect of adding both chromium and iron. In general their effect on both grain size and physical properties was additive. With iron forming a minor proportion of the mixture, the action was largely that of chromium alone. When iron was predominant in the composition, grain growth was erratic (as Gibson and Doss* found for iron alone) and at the higher annealing temperatures the grains were so unequal in size that a reasonable measurement of size could not be made.

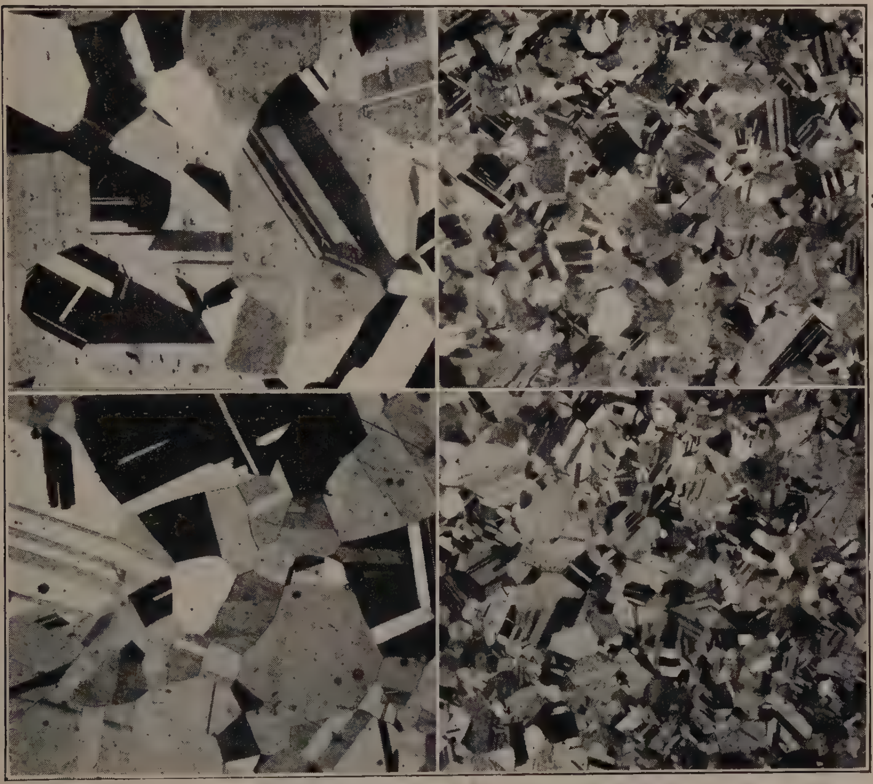

Fig. 2.—68.5 Cu:31.5 Zn cold-rolled to 50 per cent reduction and annealed 30 minutes at 750° C. × 75.
Fig. 3.—Same but containing 0.107 per cent chromium. × 75.
Fig. 4.—Same but containing 0.12 per cent iron. × 75.
Fig. 5.—68.5 Cu:31.5 Zn containing 0.065 per cent chromium, cold-rolled to 50 per cent reduction and annealed 30 minutes at 650° C.

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* Reference 1.

It was concluded that the presence of small amounts of iron in proportion to chromium was not particularly detrimental but that additions of chromium could not be depended upon to overcome the erratic influence of relatively large additions of iron.

The photomicrographs shown in Figs. 2–5 illustrate the grain size obtained by adding chromium compared with that of plain brass and of brass containing 0.12 per cent Fe. Since the annealing of drastically cold-worked brass is of greatest practical importance, the annealing characteristics of such material are presented in the various figures rather than similar data on slightly worked material.

Grain Growth on Annealing at 850° *C.*—There are some applications other than annealing, as in furnace brazing, where brass may be subjected to very high temperatures. The effect of chromium on restraining grain growth at this temperature was consequently investigated, using quarter-hard and hard-rolled brass (11 and 37 per cent reduction, respectively). Samples were suspended from a rack, which could be quickly inserted and withdrawn from an electric muffle furnace.

TABLE 2.—*Effect of Chromium on Grain Size of* 68.5 *Cu,* 31.5 *Zn Annealed at* 850° *C.*[a]

Composition	Hard-rolled Brass		Quarter-hard-rolled Brass	
	2 Min.	30 Min.	2 Min.	30 Min.
Pure brass	0.38	0.48	0.36	0.44
0.065 per cent Cr	0.30	0.38	0.40	0.44
0.107 per cent Cr	0.26	0.32	0.26	0.42
0.121 per cent Cr	0.28	0.24	0.30	0.32
0.171 per cent Cr	0.10	0.09	0.26	0.25
0.15 per cent Fe	0.36	0.50	0.38	0.50

[a] Grain size given in millimeters average diameter

Results are given in Table 2 for samples treated at temperature for 2 min. and 30 min. A 3-min. period in the furnace before the holding period was found necessary for the sample to attain 850° C.

Chromium was highly effective in retarding grain growth in cold-worked brass even when heated at 850° C. (Figs. 6 and 7). The degree of cold-work prior to annealing is a factor, the grain growth being inhibited more effectively on material that has been severely worked than on slightly worked material. For a temperature of 850° C. about 0.17 per cent Cr should be present and possibly more would be desirable if the brass is but slightly worked before heating. Iron, at least 0.15 per cent Fe, has no retarding effect whatever on grain growth at this temperature.

It is to be noted that a uniform grain size may be obtained on annealing at high temperatures when chromium is added to the brass, even though this size may be fairly large compared to that obtainable with chromium at lower temperatures. This dependability in maintaining a grain size, or this lack of sensitivity to fluctuations in temperature such as those met under operating conditions, has obvious advantages. The structure secured under high annealing temperatures with chromium, even though fairly large grained, can be uniformly reproduced; hence is for practical purposes equivalent or superior in ductility to similar structures obtained in chromium-free brasses on annealing at lower

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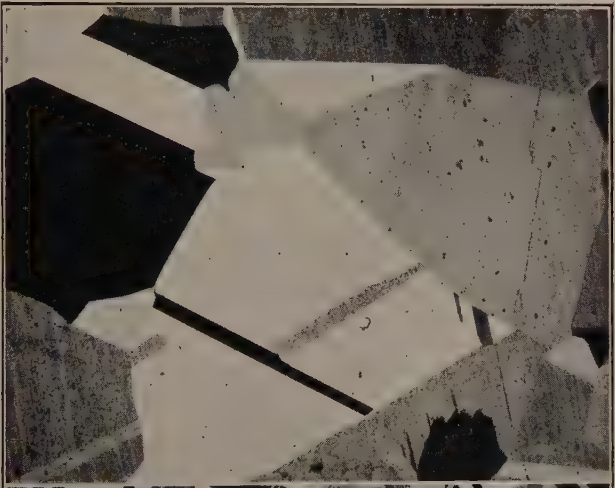

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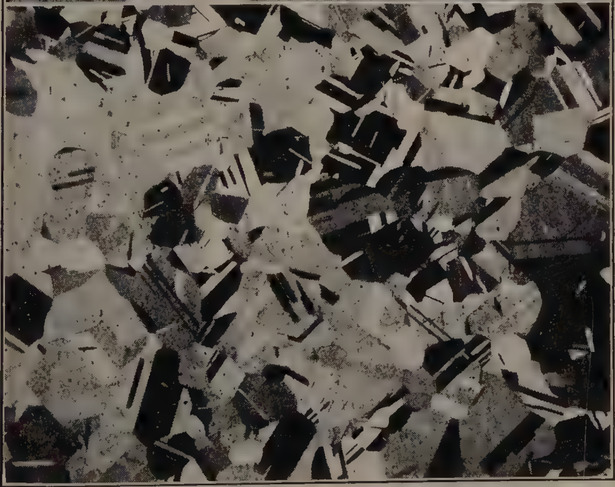

Fig. 6.—68.5:31.5 brass annealed for 30 minutes at 850° C. after 37 per cent cold reduction. × 75.

Fig. 7.—Same containing 0.171 per cent chromium. × 75.

temperatures, but of less uniform grain size, owing to greater sensitivity to temperature variations.

Effect of Chromium on Mechanical Properties

The change in mechanical properties of drastically cold-rolled brass with increasing amounts of chromium, and after annealing for ½ hr. at various temperatures, is shown in Fig. 8. From these and other tests showing the behavior of chromium brasses after cold-working to a reduction of from 0 to 50 per cent, it is concluded that:

1. Hardness increases somewhat with increasing chromium content up to 0.17 per cent Cr, but this increase becomes negligible on cold-rolling to a 50 per cent reduction in thickness.

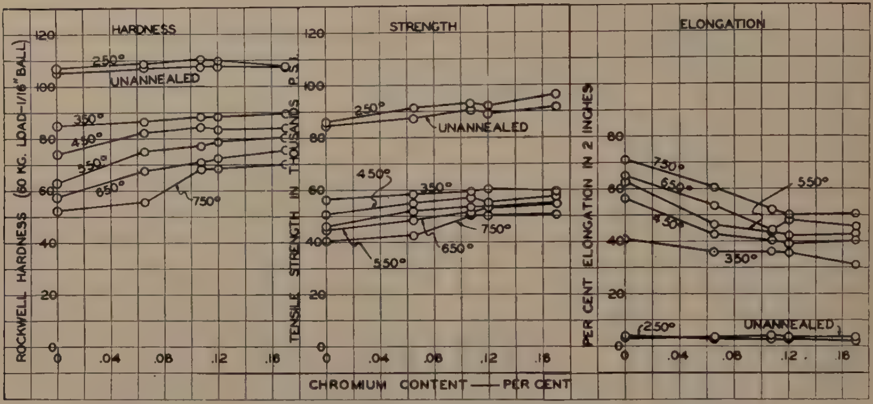

Fig. 8.—Effect of chromium on mechanical properties of 68.5:31.5 brass. The brass has been cold-rolled to 50 per cent reduction in thickness and annealed for one-half hour at various temperatures.

2. The tensile strength increases proportionately with increasing chromium additions up to about 0.12 per cent Cr. This increase amounts to about 12,000 lb. per sq. in. for the 0.12 per cent Cr brass as annealed or as cold-rolled up to 37 per cent reduction.

3. Elongation decreases with increasing chromium content up to about 0.12 per cent for annealed or slightly worked brass, but is little affected after cold-rolling to a thickness reduction of 37 per cent or more.

4. Olsen cup tests indicate that the addition of chromium to brass slightly increases the stress necessary to effect rupture, but does not permit quite as deep a draw as is obtainable with pure brass alone. This is compensated by the finer grain of the material containing chromium. For equal grain sizes, approximately equal depths of draw are obtainable, with greater tensile strength obtainable with the brasses containing chromium. Because of the wide temperature range over which the grain size changes but slightly, drawing conditions and grain size should be much more readily controlled under mill conditions when chromium is present.

In cold-rolling the brass to thin sheet, no difficulty whatever was encountered with edge cracking or defects that could be traced to the presence of moderate amounts of chromium. Although the hardness of the annealed brass is increased with increasing additions of chromium, as shown in Fig. 8, little difference in hardness and ductility can be detected after cold-working to 50 per cent reduction. It is doubtful whether the addition of 0.10 or 0.15 per cent chromium would have enough effect on cold-rolling to be noticed in the mill. No tests were made on the effect of chromium in hot-rolling brass, as a 70:30 brass is normally not hot-worked.

CONCLUSIONS

Small amounts of chromium added to 70:30 brass are exceptionally effective in retarding grain growth even at 850° C. This unusual property of inhibiting grain growth at high temperatures should be valuable not only for rapid annealing work but when brass articles must be heated to high temperatures, as in brazing or as part of an assembly that must undergo high-temperature treatment. With chromium present, far greater uniformity in grain size should be obtained in practice, even with wide fluctuation in annealing temperature, than with plain brass. A higher strength as well as small grain size should usually outweigh any reduction in ductility. Where deep drawing is involved, the desired grain size can be more readily achieved.

Only about 0.05 to 0.06 per cent Cr is needed to give a grain size of less than 0.02 mm. to brass annealed at or below 550° C.; about 0.10 per cent effectively holds the grain size below 0.04 mm. when annealing at temperatures up to 750° C. and 0.17 per cent Cr is satisfactory for restraining grain growth at 850° C. Brass containing chromium does not exhibit an erratic annealing behavior, as has been observed with iron.

ACKNOWLEDGMENT

The authors are indebted to Dr. A. B. Kinzel, of the Union Carbide and Carbon Research Laboratories, and to Dr. H. W. Gillett, of Battelle Memorial Institute, for counsel in this research. The assistance in the experimental work of Messrs. J. T. Gow and R. O. Stith of Battelle Memorial Institute is likewise appreciated. Credit is also due Mr. M. G. Corson, whose prediction of these results without prior experimentation prompted this investigation.

DISCUSSION

(Frances Hurd Clark presiding)

H. L. BURGHOFF,* Waterbury, Conn. (written discussion).—As the authors state, the effect of chromium with regard to grain growth of brass subjected to very high-temperature heat-treatments may be of considerable value, but its value in ordinary processing may be questionable. The brass metallurgist is careful to keep impurities in deep-drawing brasses as low as possible in order to control grain size satisfactorily and to obtain an optimum combination of grain size and ductility. The quality of ductility is very important in such material and any additions that reduce ductility are generally avoided even though they may produce some slight increase in strength

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* Chase Brass and Copper Co.

Consideration of Fig. 8 shows that the elongation of annealed material decreases markedly as chromium content increases. It shows, in fact, that the high ductility of the pure brass cannot be attained over a wide range of annealing temperatures by any of the chromium-containing brasses.

Another factor may enter into consideration of such alloys; that is, the actual alloying. For example, a brass containing 0.05 or 0.06 per cent Cr is pointed out as being desirable, but this might involve difficulty in actual control of chromium content, with attendant variation in characteristics.

In other words, one may get into more difficulty than one is trying to avoid in fluctuation of grain size. Also, mention may be made that annealing equipment has been considerably improved in the last few years and this variation in grain size of brass may not be so important in the problem as it was formerly.

J. L. Christie,* Bridgeport, Conn.—As a practical mill man, I, like Mr. Burghoff, rather shy away from the idea of adding what both he and I probably would call "impurities" to accomplish a result that can be accomplished in another way.

I should like to know whether the authors' notes include a record of the grain sizes of the various bars during the process of producing the metal 0.040 in. thick. I cannot speak for the effect of chromium, but with iron the grain-refining effect is definitely cumulative. The grain size obtained from a given anneal depends not only on the composition of the piece of brass, but also upon the coarseness or fineness of grain of the brass as the result of the next preceding anneal. A difference in iron content, sufficient only to produce a slight difference in grain size after one anneal, will produce an appreciable difference in grain size after a series of anneals. The evidence is that in thin metal in which a fine grain is desired, the difference between 0.01 and 0.035 per cent of iron is enough to cause an appreciable difference in grain size of the finished metal.

A. B. Kinzel,† New York, N. Y.—It would be well to point out that the chromium content is not highly sensitive. The curve shows that from 0.06 to 0.15 per cent Cr, a temperature range from 450° to 550° gives the same grain size. As for chromium being an "impurity" and not being able to control the exact amount, the limits are so wide that such control should not be a difficult problem. As a matter of fact, even if the limits were not so wide it would not be a great problem. Chromium copper-base alloys are being made regularly with the chromium held to tolerances of this order and better.

Regarding the matter of ductility, it should be emphasized that, as Mr. Gonser has pointed out, ductility is a function of grain size, and if there is a wider temperature range over which to get a given grain size the chances of getting it accurately in a manufacturing operation are greater.

There is a marked difference between the behavior of chromium and iron, as shown in the printed paper.

Member.—What theories have the authors for the mechanism of the grain growth?

B. W. Gonser.—It is true, of course, that the addition of chromium to brass increases the strength and decreases the elongation somewhat. Thus, at a given base annealing temperature the presence of a little chromium will decrease both grain size and the elongation as compared to pure brass. If annealing is done at a higher temperature, however, whether from necessity, convenience or accident, the chromium-containing brass may have just as high an elongation and as small a grain size as produced in a chromium-free brass at the lower base annealing temperature. In other words, no appreciable loss in elongation or increase in grain size need be suffered when annealing at a higher than normal temperature, if chromium is present.

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* Metallurgist, Bridgeport Brass Co.

† Chief Metallurgist, Union Carbide and Carbon Research Laboratories.

A small amount of chromium does have a drastic effect on reducing the grain size but, fortunately, above a certain minimum for each annealing temperature (Figs. 1 and 8) the change brought about by addition of more chromium becomes unimportant. Owing to this lack of sensitivity, as Dr. Kinzel has pointed out, a fairly wide range of chromium could be permitted, as from 0.08 to 0.16 per cent at medium annealing temperatures, without greatly changing the product. Control of the chromium content in such a range would not seem to be impractical. In these tests we found no great difficulty in adding chromium and getting the composition desired.

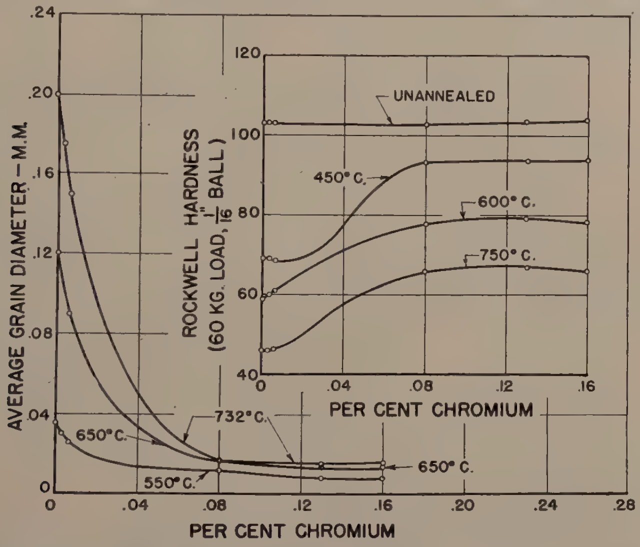

Fig. 9.—Effect of chromium on average grain diameter and on Rockwell hardness of 85:15 brass, annealed for one-half hour at various temperatures.

In reply to the question about following the change in grain size as the material was worked, we were interested only in obtaining the final brass sheet as it is normally produced in brass-mill practice, and therefore no attempt was made to follow the change in grain size at the various rolling annealing stages. Throughout this work the effect of iron, as well as of chromium, was followed in order to make direct comparisons. In Fig. 1 exactly the same treatment was given for the brass containing iron and that containing chromium. The effect of iron on the physical properties, other than grain size, was not presented in this paper, since iron in brass has been well covered by previous investigators. It has been necessary to add a relatively large amount of iron to produce much effect on the grain size at medium and high annealing temperatures and its behavior has always been considered to be erratic. Chromium appears to be much more dependable in its action.

The behavior of chromium in reducing the grain size of annealed 70:30 brass has been presented as a typical effect. Some additional work along similar lines was done with 85:15 brass to broaden the scope of this investigation.

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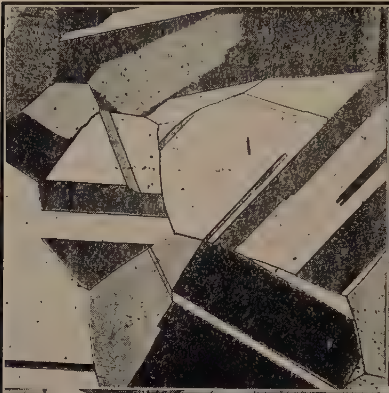

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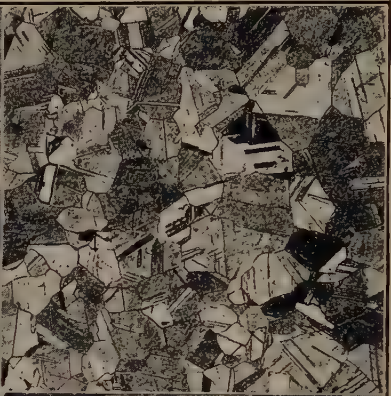

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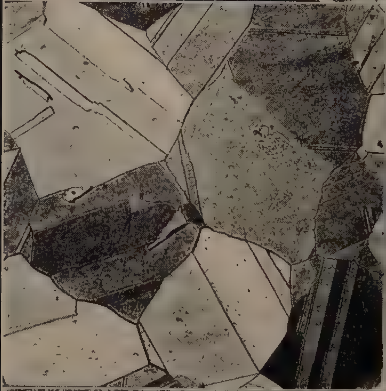

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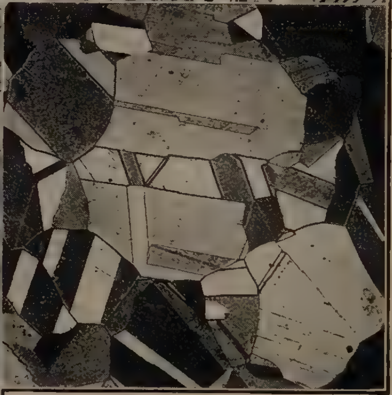

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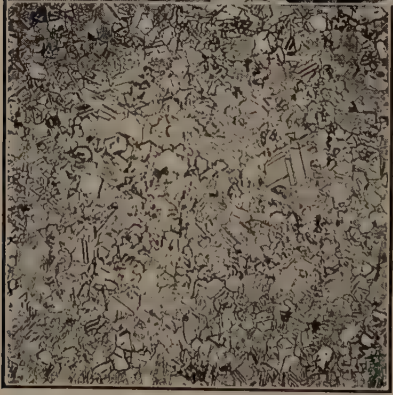

Fig. 10.—85:15 brass cold-rolled to 50 per cent reduction and annealed for one-half hour at 850° C.

Fig. 11.—Same brass as in Fig. 10, containing 0.13 per cent chromium.

Fig. 12.—85:15 brass cold-rolled to 50 per cent reduction and annealed for one-half hour at 732° C.

Fig. 13.—Same brass as in fig. 12, containing 0.006 per cent chromium.

Fig. 14.—Same brass as in fig. 12, containing 0.08 per cent chromium.

All × 75.

In this work, the same procedure was followed as has been outlined for 70:30 brass, except that it was found desirable to hot-roll the material in the early stages before cold-rolling. The strip was cold-rolled from 0.250 in. thick to the finished size, 0.040 in., with the customary 800° C. anneals of one hour each.

Fig. 9 shows the average grain diameter plotted against percentage of chromium for three different annealing temperatures. On the same graph the Rockwell hardness is plotted against the chromium content. It can be seen at once that very small amounts of chromium are able to make a tremendous decrease in grain size at high annealing temperatures. Even the effect of 0.006 per cent Cr is noticeable. The increase in hardness with chromium content is approximately the same as in the 70:30 brass.

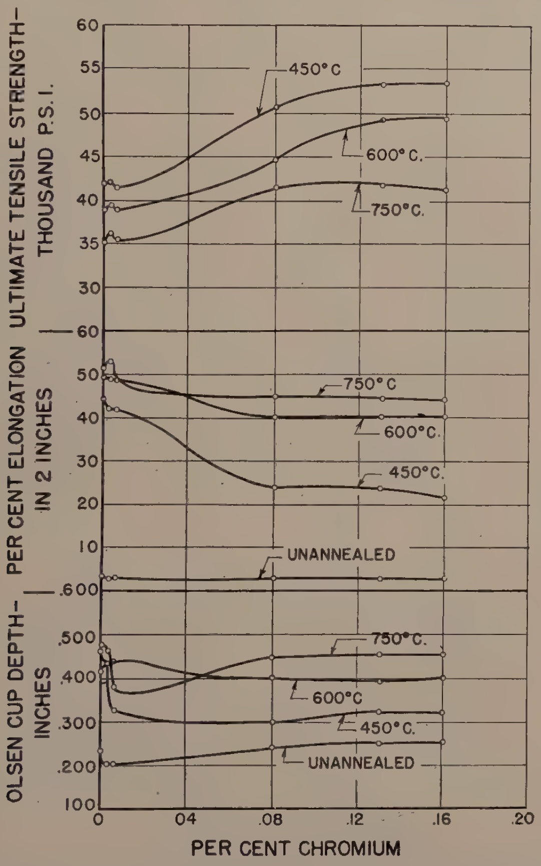

FIG. 15.—EFFECT OF CHROMIUM ON SOME MECHANICAL PROPERTIES OF 85:15 BRASS. The brass has been cold-rolled to 50 per cent reduction in thickness and annealed for ½ hr. at various temperatures.

Figs. 10 and 11 are photomicrographs of 85:15 brass with no chromium and with 0.13 per cent Cr respectively; both samples were annealed for ½ hr. at 850° C. Figs. 12, 13 and 14 show a series annealed at 732° C. with the chromium contents of nil, 0.006 and 0.08 per cent, respectively. Comparing these results with those obtained with 70:30 brass, it can be seen that a given percentage of chromium has an even more drastic effect in reducing the grain size of 85:15 brass.

Fig. 15 shows ultimate strength, percentage elongation and Olsen cup depth plotted against the chromium content. The results are closely similar to those obtained with 70:30 brass: the tensile strength rises to about 0.12 per cent Cr, while the elongation falls off somewhat, particularly at 450° C. The Olsen cup results, however, are markedly different from those obtained with 70:30 brass. There is a tendency for erratic behavior with very small percentages of chromium, but with more than 0.04 per cent Cr, the Olsen cup depths are little changed by the chromium content and are then improved in certain cases.

Summing up, it may be said that the effect of chromium in 85:15 brass is, in general, very similar to its behavior in 70:30 brass. Two differences are noted, however; one is the more powerful effect of chromium in reducing the grain size in 85:15 brass as compared to 70:30 brass and, second, Olsen cup tests indicate that the deep-drawing properties of 85:15 are only slightly affected by the chromium content, at least up to 0.16 per cent.

It is hoped that these results concerning the effect of chromium on two brass compositions will prompt others to make similar investigations with other compositions and other alloys. There can be little doubt that the effect of adding chromium to a wide range of copper alpha solid solutions should produce effects similar to those described here. It is particularly hoped that someone will actually determine in the mill the effect of chromium on deep-drawing properties and clear up this important point. Instead of considering chromium as an undesirable impurity, since little was known of its effect, it is hoped that the presence of chromium may be regarded as definitely beneficial under many conditions.

In regard to the mechanism of grain growth inhibition by chromium, one can only theorize on the basis of the data available at present. It is probably a fair assumption that the chromium is dispersed at random throughout the brass, in the form of fine particles. Many of these particles would be in the grain boundaries and hence would obstruct grain growth.

Studies upon the Corrosion of Tin, I—Potential Measurements on High-purity Tin in Carbonate Solutions

By Gerhard Derge,* Junior Member A.I.M.E.

(New York Meeting, February, 1938)

A series of studies of the corrosion of tin is under way in the Metals Research Laboratory at the Carnegie Institute of Technology. The complete program includes examination of the corrosion properties of high-purity tin and the changes produced in these properties by the addition of varying amounts of alloying elements. Other studies of this subject have been made recently under the sponsorship of the International Tin Research and Development Council, but these researches have been confined largely to the weakly acid environments commonly encountered in the canning industry.[1] There is little information available regarding the corrosion of tin under alkaline conditions, but such data would be of value, for a large amount of the metal is used under such conditions.

The potential measurements to be described were made because they seemed to offer the most rapid method for obtaining a general view of the conditions to be encountered in such service. These experiments will also serve to establish a technique that will be of value in further studies. It must be emphasized that the results reported are those of controlled laboratory experiments and that the conclusions drawn cannot yet be applied to service conditions; rather, they point to the directions in which more exhaustive experimental work may be done to best advantage.

Experimental Procedure

The first work was devoted entirely to the problem of obtaining reproducible results from a series of potential measurements. Only the methods finally adopted as standard will be described here, except when the variations from these have furnished results of interest.

The cell used is shown schematically in Fig. 1. The electrolyte is contained in the vessel *A* (an inverted bell jar), whose ground top is fitted to the transite-board lid *B*. The controlled atmosphere can be admitted

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Manuscript received at the office of the Institute Dec. 1, 1937.

* Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

[1] References are at the end of the paper.

and withdrawn through the side tubes *T* and *T′*. The potential of the tin specimens (Sn) is measured against a saturated calomel half cell, connected through the agar salt bridge *S*, by means of a Leeds and Northrup student type potentiometer. All potentials are reported with reference to the calomel cell. The salt bridge enters the center of the cell and five tin electrodes are spaced symmetrically in a circle about it.

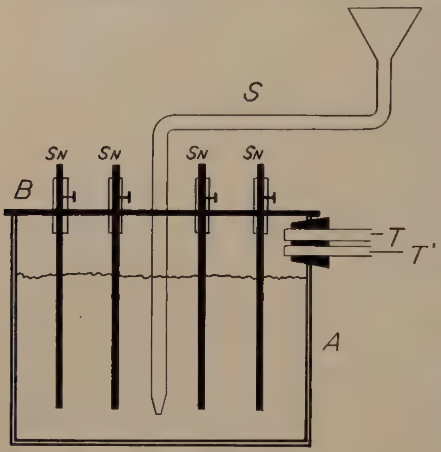

Fig. 1.—The electrolytic cell.

The atmosphere was supplied from the laboratory air line and bubbled through two bottles of sodium hydroxide solution and one of glass wool.

The chemicals were all of C.P. quality. The following electrolytes were prepared and their pH values measured with a hydrogen electrode:

	pH
1. 0.1 M $NaHCO_3$	8.4
2. 2 parts 0.1 M $NaHCO_3$, 1 part 0.1 M Na_2CO_3	9.5
3. 1 part 0.1 M $NaHCO_3$, 2 parts 0.1 M Na_2CO_3	10.0
4. 0.1 M Na_2CO_3	11.2
5. Each of these electrolytes made 0.001 M with NaCl.	

The agar bridge was filled with the same electrolyte that was used in the cell. A freshly prepared bridge was used for each experiment.

The electrodes were made from two different ingots of Chempur tin.* Cut sections were hand-rolled to a thickness of 2 mm., pickled in concentrated hydrochloric acid to remove possible contamination, and then cut into electrodes 7 by 1 sq. cm. One surface of each sample was polished with No. 1 emery paper. Samples were then sealed into a Pyrex tube evacuated to less than 0.5 micron, protected from the mercury diffusion pump by a carbon dioxide-acetone freezing trap. The sealed samples were annealed for 2 hr. at 210° C. by immersion in boiling nitrobenzene. The tubes were opened 24 hr. before use and the electrodes stored for this period in a desiccator containing calcium chloride. The surface prepared in this way was used and will henceforth be designated as standard. Surfaces prepared by other methods were studied and will be described later in the paper. Before mounting in the cell, the backs and edges of each electrode were covered with paraffin. The electrodes were then mounted so that about 5 sq. cm. of surface was exposed to the electrolyte by partial immersion.

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* A typical analysis of this grade of tin is reported in the Statistical Year Book 1937 of the International Tin Research and Development Council: purity, 99.9919; Sb, 0.003; As, nil; Pb, 0.0027; Bi, 0.0006; Cu, 0.0005; Fe, 0.0013; Ag, nil; S, trace.

EXPERIMENTAL DATA

Reproducibility of Data.—Any other than the standard treatment, such as final polishing on 00 emery paper, cathodic treatment, or pickling in hydrochloric acid after polishing, gave highly divergent results in supposedly identical samples. The results obtained from the standard surfaces, however, were quite consistent qualitatively, and often in good agreement quantitatively. Fig. 2 shows the time-potential curves for the five samples run simultaneously in $NaHCO_3$ electrolyte, while Fig. 3 is a similar set of curves from Na_2CO_3. In the entire series of solutions listed above, better reproducibility was obtained as the pH values increased. Some experiments were continued for as long as five days, and these measurements showed that the curves do not change significantly after the first 24 hr. In view of the good agreement among the several curves taken under identical conditions, subsequent figures will show only one curve, which is typical of the five curves obtained. Unless otherwise stated, the results reported have been checked by at least two different runs of five samples each, and often specimens from the two different lots of Chempur tin were included.

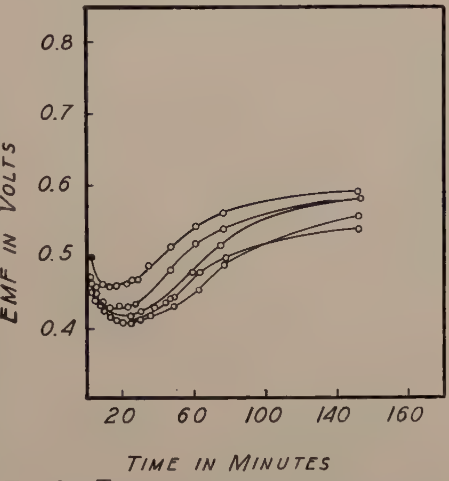

FIG. 2.—TIME-POTENTIAL CURVES OF STANDARD SURFACES IN 0.1 M $NaHCO_3$. Electromotive force referred to saturated calomel cell.

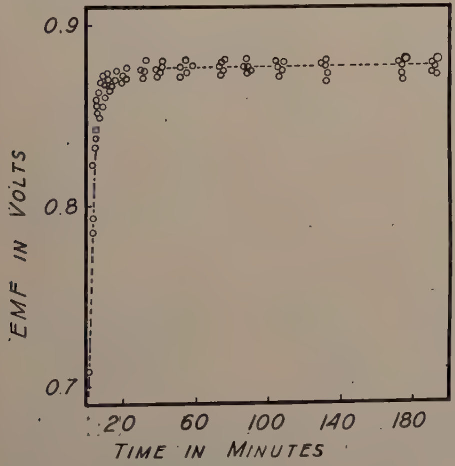

FIG. 3.—TIME-POTENTIAL CURVES OF STANDARD SURFACES IN 0.1 M Na_2CO_3. Electromotive force referred to saturated calomel cell.

Effect of pH.—The steady-state potential, approached by each sample with time, increases with increasing pH, as shown by Fig. 4. The electrolyte with pH 12.6 was prepared by making the electrolyte of type 1 (pH, 8.4; 0.2 M with NaOH).

Effect of Oxide Films.—Oxide films were produced artificially by four different methods, as follows: (1) annealed in air at 110° C. for 95 hr.; (2) annealed in air at 175° C. for 22½ hr.; (3) annealed in air at 210° C. for 8 hr.; (4) anodic oxidation in an electrolyte containing sodium phosphate and phosphoric acid.[2]

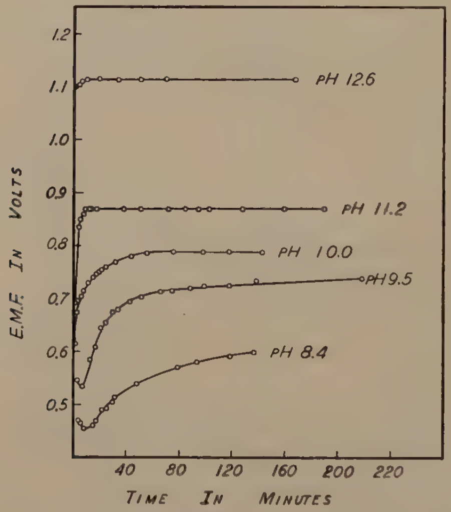

Fig. 4.

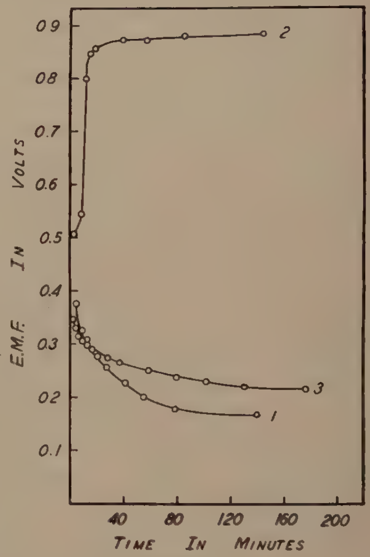

Fig. 5.

Fig. 4.—Time-potential curves related to pH values.
Electromotive force referred to saturated calomel cell.

Fig. 5.—Time-potential curves of surfaces covered with oxide films.
Electromotive force referred to saturated calomel cell.
Curve 1. Sample annealed in air at 110° C. for 95 hr., measured in 0.1 M $NaHCO_3$.
Curve 2. Sample annealed in air at 110° C. for 95 hr., measured in 0.1 M Na_2CO_3.
Curve 3. Sample annealed in air at 210° C. for 8 hr., measured in 0.1 M Na_2CO_3, 0.001 M NaCl.

The characteristics of these films are summarized in Table 1 and Fig. 5. It is noteworthy that the film produced by annealing at 210° C. is protective in all solutions studied.

Effect of Chloride Ion.—All of the experiments described above were repeated in electrolytes that had been made 0.001 M in chloride ion by the addition of sodium chloride. Within the limits of accuracy of the experimental method, these curves were the same as those obtained from chloride-free electrolytes.

Microscopic Observations.—The tin electrodes used in these experiments were observed microscopically before and after the potential measurements. Samples that had become passive during the measurements appeared either the same as when immersed or slightly stained, while those that had become active showed an etched surface without any evidence of film formation.

TABLE 1.—*Characteristics of Oxide Films*

Type of Film	Type of Electrolyte	Observation
Annealed in air at 110° C. for 95 hr.	0.1 M $NaHCO_3$	Five samples became passive and remained so for 7 days. See Fig. 5, curve 1.
	2 parts 0.1 M $NaHCO_3$, 1 part 0.1 M Na_2CO_3	Five samples became passive.
	1 part 0.1 M $NaHCO_3$, 2 parts 0.1 M Na_2CO_3	Three samples became passive, two samples became active.
	0.1 M Na_2CO_3	Five samples became active. See Fig. 5, curve 2.
Annealed in air at 175° C. for 22½ hr.	0.1 M Na_2CO_3	Five samples became passive and remained so for 2 days.[a]
Annealed in air at 210° C. for 8 hr.	Each of the above made 0.001 M with NaCl	All samples became passive. See Fig. 5, curve 3.
Anodic oxidation in an electrolyte containing Na_2HPO_4 and H_3PO_4	0.1 M Na_2CO_3	Five samples first became passive, but then turned active within 24 hours.[b]

[a] Experiment discontinued at this time.

[b] These films were originally adherent, but could be rubbed off easily at the conclusion of the experiment.

SUMMARY

1. Potential time curves have been determined for uniformly prepared surfaces of Chempur tin in $NaHCO_3$ and Na_2CO_3 solutions.
2. The tendency of the material to corrode, as measured by potential values, increases with increasing alkalinity.
3. Oxide films produced by annealing in air prevent the specimens from becoming electrochemically active.
4. The behavior of the material is not influenced by chloride ion when present in 0.001 M concentrations or less.

ACKNOWLEDGMENTS

The author is indebted to Dr. J. C. Warner for his cooperation during this work and to Messrs. R. M. Kirk and H. Markus for experimental assistance.

The Bristol-Myers Co., of New York City, has sponsored the research program of which this investigation is a part.

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2. R. Kerr and D. J. Macnaughton: Production of Black Anodic Coatings on Tin and Tin Alloys. *Jnl.* Electrodepositors Tech. Soc. (1937) **12**; International Tin Research and Development Council, series A, *Tech. Pub.* No. 48.

DISCUSSION

(*R. M. Burns presiding*)

R. M. Burns,* New York, N. Y.—This paper considers the corrosion of tin in terms of the electrical potential of tin in certain solutions and the change in potential with time. As everyone knows, a considerable amount of effort has been and is being devoted to corrosion testing of the change-in-weight type. More recently the realization that corrosion is an electrochemical reaction, at least in presence of moisture, has led to the use of electrochemical methods of investigation. Current and time-potential studies have been employed in the investigation of the corrosion of iron, lead, aluminum and other metals. Even the corrosion behavior of steel surfaces beneath coatings of paint have been studied by these techniques. T. P. Hoar has lately used these methods most effectively in studies on the corrosion of tin. Dr. Derge's paper is a further application of this technique.

R. B. Mears,† New Kensington, Pa.—Dr. Derge's paper describes some very accurate and interesting work. The high reproducibility of his results indicates that a very satisfactory technique must have been worked out for preparing and measuring the specimens. It is important that the author observed that the specimens that gave falling time-potential curves did not become attacked, while those giving rising curves were etched; therefore it is permissible for the author to refer to specimens giving the first type of curve as becoming passive and those giving the second type of curve as becoming active. However, it should be stressed that a falling curve does not necessarily indicate the occurrence of passivity (if passivity means substantial freedom from attack) but only that the polarization of local anodes on the surface of the specimen is increasing more rapidly than the cathodic polarization. Similarly, a rising curve does not mean that the rate of attack of the specimen is increasing, but only that polarization of the local cathodes on the specimen is increasing faster than anode polarization; therefore it is important that all single potential measurements of this type be supplemented by observation as to the amount of attack on the specimens themselves.

H. F. Moore,‡ Urbana, Ill.—My question is a question, not a criticism. I noticed that as the passivity action, whatever is the cause of it, increased, the author referred to its connection with the properties of the film. Would it be a feasible field of research to see whether this passivity was connected in any way with the mechanical strength, mechanical ductility of a possible combination, which we may call the toughness of the film? Such a research might have a great deal of bearing on that most alarming phenomenon of corrosion fatigue and of corrosion stress in general.

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* Bell Telephone Laboratories.

† Aluminum Research Laboratories.

‡ Research Professor of Engineering Materials, University of Illinois.

R. M. Burns.—This type of approach to the corrosion problem should be encouraged. While it is true that this technique reveals nothing concerning loss of weight and is not in that sense a quantitative method, it does provide the sort of information that enables one to understand corrosion behavior. Relatively too much emphasis has been placed upon the importance of quantitative measurements in corrosion research. It is much more important to know what the mechanism of corrosion is under certain definite conditions than to know that a certain amount of corrosion occurred in a given time. Such information enables the chemist or engineer to design protective and preventive measures intelligently.

One point that I would like to raise is the convention of the sign of the electrode, which is always with us whenever electrolytic potentials are represented. I believe the author has chosen the thermodynamic school for his convention, which is, therefore, a little confusing to those who follow the convention of the Electrochemical Society, the Faraday Society and the International Critical Tables, in which zinc is taken as electronegative and gold as electropositive. Inasmuch as most other investigators in the field adhere to this established convention, it would seem desirable in the present study.

T. A. Wright,* New York, N. Y.—My observations are not as detailed as I should like, because they are derived from certain work in which the samples come in at one o'clock from a client that is in trouble and the answer is supposed to be ready for him at four.

In making certain studies of materials, both of the cosmetic and of the food type, in which tinfoil, either of the ordinary grades of refined tin or with some alloy constituent, has been used as the tubing or sheathing, for example, we have made one observation that was very helpful at one time. In dealing with a white material, which happened to be alkaline, exposure under the iron spark disclosed incipient corrosion attack of the tin container; we have pretty definite proof of that, because on others in which time had been more prolonged the darkening effect was noticed, which was not observed any other way.

The other observation, which perhaps might be still more helpful, is that in dealing with foods or cosmetics of a solid character containing considerable moisture, it is possible to section these foods, say in millimeter sections. In studying those sections from center to contact with the tin container, it is possible to observe a steadily decreasing amount of tin in the food or cosmetic as the center is approached. It is possible, also, at times to study selective attack of tin alloy by that method. In general, we find it is the tin that diffuses. It will go a considerable distance, and will be high at contact and fairly evenly decreased until it comes to the center.

G. Derge (written discussion).—In answer to Professor Moore's question, I think corrosion-fatigue is more closely related to the perfection of the oxide film than to its mechanical strength, although some correlation of these two properties might be possible if satisfactory methods of measurement were available.

H. F. Moore.—Ought not the two be tied together?

G. Derge.—I should think so.

In answer to Mr. Wright's discussion, we appreciate very much observations of this sort from actual experience when we are trying to make a purely laboratory study of corrosion. We have made the same observation that he has in sectioning some tin tubes in which the contents had solidified and we found there was a considerable diffusion of tin into the material and very little diffusion of the other alloy elements in the tubes.

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* Secretary and Technical Director, Lucius Pitkin, Inc.

An Investigation of the Physical Properties of Wirebars of Electrolytic Copper

By M. G. Corson*

(New York Meeting, February, 1938)

Until recently, the characteristics of cast copper have seldom been studied and such study as has been made has been inadequate. The prevailing idea seems to be that since pure copper is infrequently used in the cast state, there is no reason for trying to establish precise data regarding the properties of the metal in that condition. On the other hand, wrought copper either in the shape of sheets or wire rarely fails in service, except as a result of the action of reducing gases at the annealing temperatures, so there is little incentive to study the properties of the cast shapes —cakes, bars, ingots and billets—for the sake of tracing the causes of failures of the wrought metal to the cast stock.

However, about a decade ago, wirebars of American origin often cracked badly while being hot-rolled in mills in Germany. This led to four investigations: by E. Seidl and E. Schiebold,[1] by P. Siebe,[2] by O. Bauer and G. Sachs,[3] and by G. Welter.[4] These authors came to the conclusion that failures in hot-rolling were due essentially to the presence of a wide zone of columnar crystals between the thin layer of fine crystals near the surfaces of the bars and the large but more nearly equiaxed grains of the central core. This macrostructural defect was explained in turn by the probable upward deviation in the temperature of the metal while it was being poured into the molds of the casting machine.

More recently, cast shapes of copper were investigated by N. P. Allen[5] and by C. Blazey.[6] Allen examined vertically cast wirebars and horizontally cast wedge cakes of electrolytic tough-pitch copper, but only for the distribution of densities; i.e., porosity. Blazey was interested mainly in the mechanism of the variations in electrical conductivity due to cold-work and anneal, but gave introductively an account of the composition and average densities of the tough-pitch horizontally cast wirebars used. As far as the present writer can tell, no investigation was undertaken for the sake of presenting a picture of the distribution of mechanical characteristics in the wirebars of copper, tough-pitch or otherwise.

Manuscript received at the office of the Institute Dec. 15, 1937.

* Consulting Engineer, New York, N. Y.

[1] References are at the end of the paper.

It may be reasoned, of course, that the knowledge of porosity distribution suffices to predict the possible distribution of characteristics. Qualitatively, this may be so. It is almost obvious that a bar with an average density of 8.58 or a porosity of 4 per cent may not be as good as one with a density of 8.77, or a porosity of only 2 per cent.

Imagine, on the other hand, an ingot with an average density of 8.30; a rather low figure, corresponding to a porosity of nearly 8 per cent. Suppose further that this porosity is fairly evenly distributed in bubbles of 0.1-mm. diameter among grains of copper 1 mm. in diameter; i.e., fine enough. In such a bar, the characteristics could hardly differ by more than 8 per cent from those of a 100 per cent sound metal. Had the sound bar shown, for example, an ultimate strength of 32,000 lb. per sq. in. and 55 per cent elongation, no one would think of rejecting as unsound another bar showing 29,600 lb. per sq. in. and 51 per cent elongation. As a matter of fact, however, wirebars and cakes with an average specific density of 8.30 have little chance of remaining sound when passing through the rolling mill. It is evident, then, that the bulk distribution of porosity cannot in itself define the characteristics of the metal and its fitness for the rolling process. The situation is far more complex than that.

It is the writer's intention to discuss the characteristics of cast copper, even though he was not able to go beyond the domain of the wirebars. For this purpose he investigated a bar of tough-pitch copper having a most normal flat set, and compared its characteristics with those of an oxygen-free, gas-free wirebar vertically cast. Both bars were 4 in. thick, but the tough-pitch bar was, naturally, trapezoidal in its cross section, the upper surface being 4½ in. wide.

THE TOUGH-PITCH WIREBAR

Fig. 1 shows the macrostructure of a tough-pitch bar. The layer of columnar crystals was not very wide, and the crystals in it rather small in cross section. The zone of fine crystals was extensive, but there was also a zone of very large crystals emanating from a point about 1 in. below the upper surface and reaching comparatively far in every direction. However, comparison with the macrostructures of wirebars that rolled well in the tests made by the German investigators indicates that the present bar would also have rolled well.

This bar was cut transversely into a number of chunks 6 in. long and a number of cakes about 1 in. thick. The chunks were then cut longitudinally, yielding 16 bars each. Most of these served to prepare tensile-test bars, while eight, coming from chunk numbered 5 and forming one-half of it, were machined into impact-test bars with four notches each. Of the cakes, one served for the determination of local densities and was

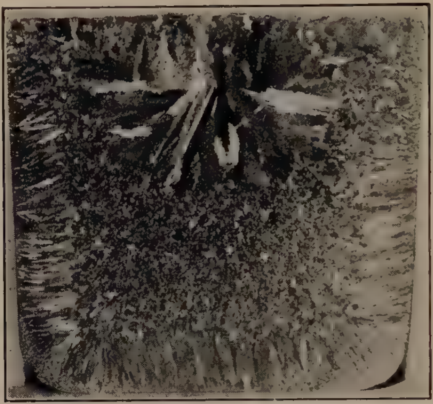

FIG. 1.—MACROSTRUCTURE OF HORIZONTALLY CAST TOUGH-PITCH BAR. AVERAGE DENSITY 8.50.

8.45	8.35	8.37	8.36	8.37	8.32	8.49
8.44	8.35	8.37	8.43	8.48	8.41	8.46
8.49	8.37	8.44	8.52	8.48	8.36	8.45
8.48	8.47	8.41	8.42	8.44	8.38	8.47
8.50	8.48	8.48	8.47	8.50	8.49	8.58
8.53	8.57	8.57	8.52	8.52	8.68	8.60
8.73	8.61	8.63	8.66	8.62	8.70	8.76

FIG. 2.—DENSITY DISTRIBUTION OF BAR IN FIG. 1.

6.0	6.4	5.6	5.4
5.6	5.6	5.2	5.8
5.0	5.2	5.0	4.6
3.6	3.5	3.9	3.0

FIG. 3.—PERCENTAGES OF POROSITY OF BAR IN FIG. 1.

21.9	18.6	$\frac{19.1}{9.0}$	$\frac{21.2}{8.8}$
18.0	20.8	$\frac{21.6}{10.8}$	$\frac{17.8}{8.0}$
20.8	21.9	$\frac{21.2}{8.3}$	$\frac{22.4}{8.9}$
24.1	22.8	$\frac{23.1}{10.0}$	$\frac{24.5}{10.3}$

FIG. 4.—ULTIMATE TENSILE STRENGTH IN 1000 LB. PER SQ. IN. AND FT-LB. IZOD OF BAR IN FIG. 1.

$\frac{21}{18}$	$\frac{18}{16}$	$\frac{15}{15}$	$\frac{17}{13}$
$\frac{14}{14}$	$\frac{19}{18}$	$\frac{25}{21}$	$\frac{13}{11}$
$\frac{22}{22}$	$\frac{17}{14}$	$\frac{14}{12}$	$\frac{24}{18}$
$\frac{32}{25}$	$\frac{27}{19}$	$\frac{31}{30}$	$\frac{29}{31}$

FIG. 5.—ELONGATIONS AND AREA REDUCTIONS OF BAR IN FIG. 1.

cut into 49 specimens (seven to a side), two were machined into test pieces (four to a cake) and two were left to yield impact-test bars.

Unfortunately, it was not possible to complete the program, and only the results of the tests made are described here. All told, 46 specimens were broken in tension and 16 in impact.

Characteristics

Fig. 2 shows the distribution of densities and Fig. 3 the corresponding porosities through the cross section of the bar. As might be expected, the lower layer, with an average porosity of 3.0 per cent, was the densest and the upper, with 6.2, the most porous. The corners of the lower layers were densest (2.0 and 2.4 per cent) and so also were the corners of the upper layer (5 and 5.5 per cent). However, the inside of the cross section showed an anomalous situation. In the two lower layers porosity increased continuously toward the center. In the next two the region of the fine crystals was less dense than the region of the rough crystalline core, although the pinholes in the latter were clearly perceptible to the naked eye.

The average density of the cross section was 8.50, which belongs to the upper values obtainable for wirebars in general.

In Fig. 3, the porosities are recalculated to correspond to the larger divisions, the centers of which were coaxial with the centers of the tensile-test bars. Figures so obtained were checked later by taking the densities of the samples cut off from the heads of the test bars before breaking the latter. No variations of more than 0.03 were recorded and it can be stated that a wirebar is likely to be of a uniform density along each line parallel to its longitudinal axis.

TABLE 1.—*Characteristics in Transverse Direction of Tough-pitch Wirebar*

BULK DENSITY 8.50

Location of Bar	Mark	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction in Area, Per Cent
Bottom quarter	3-1	23,500	24	19
	4-1	24,200	31	21
Second quarter	3-2	23,800	26	19
	4-2	23,300	22	16
Third quarter	3-3	20,300	14	15
	4-3	21,200	17	14
Top quarter	3-4	20,400	18	15
	4-4	19,900	14	13

Two test bars were taken from the lower quarters of two cross sections 6 in. from one another. Both broke close to the center of the gauge

TABLE 2.—*Characteristics in Axial Direction of Same Bar as in Table* 1

Location of Bar	Mark	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction in Area, Per Cent
Corners of bottom quarter.........	1-7	23,000	37	26
	5-7	24,400	30	29
	6-7	25,000	30	19
	1-16	24,000	30	42
	6-16	25,000	28	21
	Average	24,300	31	27
Inner parts of bottom quarter.....	1-8	22,600	26	19
	5-8	22,300	29	18
	6-8	23,500	26	19
	1-15	23,100	33	44
	6-15	23,100	28	17
	Average	22,900	28	23
Outer parts of second quarter......	1-5	20,100	20	23
	5-5	20,300	22	27
	6-5	22,000	23	15
	1-14	22,300	24	19
	6-14	23,100	28	17
	Average	21,600	23	20
Inner parts of second quarter......	1-6	22,000	17	13
	5-6	22,200	18	15
	6-6	21,400	17	15
	6-13	21,200	14	12
	Average	21,700	16.5	14
Outer parts of third quarter.......	1-3	17,300	13	14
	5-3	16,300	13	13
	6-3	20,300	16	15
	1-12	18,900	15	15
	6-12	16,700	10	08
	Average	17,600	13	13
Inner parts of third quarter.......	1-4	20,500	16	15
	5-4	20,400	18	19
	6-4	21,500	24	21
	1-11	21,200	25	30
	6-11	22,000	24	12
	Average	21,100	21	19
Corners of top quarter............	1-1	22,500	22	19
	5-1	21,200	20	19
	6-1	21,900	20	17
	1-01	21,100	18	13
	6-01	21,300	16	12
	Average	21,600	19	16
Inner parts of top quarter.........	1-2			
	5-2	19,300	20	19
	6-2	17,900	16	12
	1-9	19,000	15	18
	6-9	19,200	15	12
	Average	18,800	17	15

length. The tensile strengths, 23,500 and 24,200 lb. per sq. in., are in close agreement, the difference amounting to 3 per cent only. Bars in the second quarter were only slightly weaker, the variation being 5 per cent. There was a decided drop in strength in the third quarter (20,800 lb. per sq. in. average) and another slight drop in the upper quarter (20,200 lb. per sq. in. average). All four upper test bars failed at a point belonging to the region of the fine crystals with an anomalous low density.

Ductility values were affected to a much greater extent. From an average elongation of 27 per cent in the lower quarter coupled with an area reduction of 20 per cent they dropped to 16 per cent elongation and 15 per cent reduction in area in the two upper quarters.

Characteristics in Axial Direction

The ultimate strength in the corner regions of the lower quarter was high and comparatively uniform. For two of the five bars tested it was 25,000 lb. per sq. in. and the average was 24,300. Elongations were uniformly good, 27 to 30 per cent, but area reductions varied between 19 and 42 per cent.

The two inside parts of the lower quarter were slightly weaker, just as they were slightly more porous. Elongations were reasonably good (average of 28 per cent), but area reductions dropped considerably. The outer parts of the second quarter averaged only 21,200 lb. per sq. in. and 22 per cent elongation; the inner parts, 21,800 lb. per sq. in. and 16.5 per cent. Area reductions varied between 15 and 27 per cent in the outer and 12 and 15 per cent in the inner quarters.

The outer parts of the third quarter had a regularly low strength of 16,300 to 18,900 lb. per sq. in., an elongation between 10 and 16 per cent, and area reductions between 8 and 15 per cent. The inner parts, of almost the same density as the outer ones, had much better characteristics. Their tensile strength averaged 21,100 lb. per sq. in., elongation 22 per cent average and reduction in area 21 per cent average, and the individual strength values obtaining along the same longitudinal line were surprisingly close.

The situation was reversed for the upper quarter; i.e., in the metal that was close to the surface of the wirebar. Here the strength of the corner part averaged 21,600 lb. per sq. in., the elongation 19.4 per cent, but the area reductions for one corner averaged 18.3 per cent and for the second corner, 15.2 per cent.

The characteristics of the inner parts were not as good, but still were better than in the outer quarters of the preceding layer. Tensile strength averaged 18,900 lb. per sq. in., elongation 16.2 per cent and area reductions 12 to 19 per cent.

Eight impact-test pieces were machined in the axial direction. Four breaks were obtained in each piece and the values did not vary beyond the

TABLE 3.—*Impact Izod Values, Tough-pitch Bar*

Location of Bar	Mark	Impact Values	Average
Corner of bottom	5-16	10.0–11.0– 9.0–11.0	10.3
Inside of bottom	5-15	11.0–10.0–10.0– 9.0	10.0
Outside 2nd quarter	5-14	9.0– 9.0– 8.5– 9.0	8.9
Inside 2nd quarter	5-13	8.5– 8.0– 8.5– 8.0	8.3
Outside 3rd quarter	5-12	8.5– 8.0– 7.5– 7.0	8.0
Inside 3rd quarter	5-11	11.0–10.0–11.5–10.5	10.8
Corner of top	5-01	9.5– 8.5– 6.5– 9.5	9.0
Inside top quarter	5-9	9.0– 8.5– 9.0– 8.5	8.8

usual amount for impact test. They corresponded only roughly to the static characteristics. Five test bars showed the low value of 8.0 to 9.0 ft-lb. These included the whole upper quarter, the whole second quarter counting from the bottom and the inner part of the third quarter (next to the top). The bottom quarter had an impact strength above 10 ft-lb., and the inner part of the third layer yielded the highest value, 10.8 ft-lb. Dynamically, it was slightly stronger than the bottom quarter; statically, slightly weaker.

Fig. 4 shows the distribution of tensile strength and impact resistance; Fig. 5, elongations and area reductions.

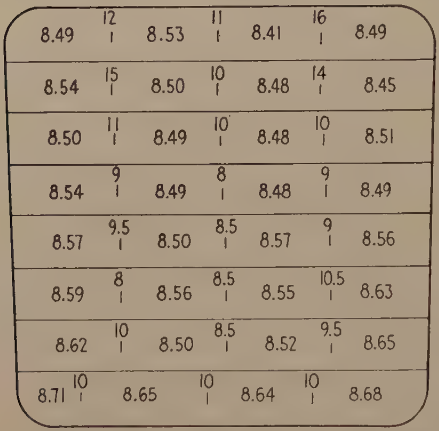

FIG. 6.—DISTRIBUTION OF SPECIFIC DENSITIES AND TRANSVERSE IZOD IMPACT VALUES THROUGH CROSS SECTION OF TOUGH-PITCH WIREBAR OF AVERAGE DENSITY OF 8.54.

Impact resistance in the transverse direction was studied from eight specimens taken from a tough-pitch wirebar of identical appearance and macrostructure but a slightly larger size. The cross section is shown in Fig. 6, together with the Izod values and the specific densities. Both characteristics show that this wirebar was of a somewhat superior quality. Its average density was 8.54, the lowest figure being 8.41, the highest 8.71.

Of the 24 fractures obtained 22 were clear breaks; but, contrary to all expectations, the spots of highest resistance did not correspond to the spots of highest density. The upper two-eighths were the strongest, showing the values of 12 to 16 Izod at their extremities. The central parts of the same bars showed only 11 and 10 Izod, but even so, they were not by any means dynamically weaker than the bottom bar, with its uniform

10 Izod, and the bar third from the top, practically identical with it in impact resistance. The remaining parts of the cross section were considerably weaker, averaging only 9 Izod.

The conclusion to be reached is that even a good tough-pitch wirebar of a high bulk density has certain longitudinal directions of low mechanical characteristics. Their location is not incidental but strictly connected to the phenomena of gas evolution during solidification. The statically weak directions correspond roughly to the distribution of low bulk densities, but must depend, logically enough, on the localized areas of porosities higher than those computed from specific density determinations.

The weak directions run in the proximity of the axis of the upper surface of the metal and also close to the side surfaces, somewhat above their central levels.

Even the lower half of the wirebar contains directions of low ductility and has a definitely low impact resistance. The bottom layer is built up of sufficiently dense metal with "good" characteristics, although the dynamic characteristics are almost as low as everywhere else. The "good" is put in quotation marks because it represents a concession. The fact is that out of 46 test bars broken in tension, not one showed even the slightest tendency to form a neck before failing. There was no visible flow of the metal and the breaking load continued to increase until fracture occurred, there being no period of a strictly plastic flow. The elongation never went above 33 per cent, while area reductions varied greatly, seldom reaching 30 per cent and mostly staying about 20 per cent.

Among all the 46 bars tested there was not one that showed slipbands, but, on the other hand, not one retained an unimpaired surface. Many incipient cracks were visible, even in the test bars taken from the bottom of the wirebar.

Fractures, both tensile and impact, exhibited many globular holes of a reddish, brilliant surface, proving that these were not shrinkage cavities but true gas holes, probably formed by gases that can produce a thin coat of oxide (steam, carbonic acid, sulphur dioxide). The gas holes averaged 0.20 to 0.30 mm. in the upper samples and 0.10 to 0.15 in the bottom ones.

It might be interesting to compare the present data with those gained from the literature mentioned earlier. This comparison will prove that the wirebar examined by the present writer belonged to the upper grades of commercial wirebars.

Seidl and Shiebold found the lowest density to be 8.31 and 8.35, respectively; the highest, 8.48 and 8.45, respectively (one American and one German wirebar). The lowest density of the bar in the present investigation was about 8.35; the highest, 8.76.

The three bars investigated by Blazey had densities of 8.38, 8.43 and 8.50. All of them rolled well. The present bar had a bulk density of 8.50.

Welter recorded a strength of 12,400 lb. per sq. in. and elongation of 12 per cent. His highest were 26,400 lb. per sq. in. and 29 per cent; two other figures were 21,300 with 29 per cent and 23,000 with 24.5 per cent. Except for the highest value shown, the other three are well within the results of the present investigation.

Vertically Cast Wirebar Not Fully Degasified*

Fig. 7 shows the macrostructure of a 4 by 4-in. bar and Fig. 8 the distribution of densities. It is interesting to note that while only a single section of all the 49 had a porosity as low as 2.2 per cent, the very center of the bar had a porosity of 2.9 per cent only, as against the average 2.7 per cent for the corner sections, where the highest density could be expected. The eight sections next to the center averaged a porosity of 3.2 per cent with only one section showing 3.9 per cent. It can be said, therefore, that the bar under examination was almost uniformly dense.

A chunk of this bar was cut parallel to its axis into 16 sections, half of which were used for tensile tests and half for impact tests. The results are reproduced in Table 4. It can be noted immediately that the tensile strength changes little, averaging 23,000 lb. per sq. in. with a variation of −4 and +5 per cent. Elongations also varied but slightly from the average of 28.5 per cent. Area reductions varied more, but the average was 26 per cent and the lowest 20 per cent.

Impact strengths were considerably higher than for the tough-pitch bar. The lowest average of 11.5 ft-lb. came from the outside bar, which had the highest porosity, 3.4 per cent. The corner bars, with porosities of 2.8 and 2.9 per cent, had an impact resistance of 14.2 and 13.5 ft-lb. In the five other bars the impact resistance, varying between 11.9 and 13.4 ft-lb., could not be connected at all with the average porosity in the corresponding direction.

Figs. 9 and 10 show the distribution of porosity, strength, impact resistance, elongation and area reduction through the cross section.

Undoubtedly the bar in question would have rolled acceptably for commercial purposes. However, in spite of its superior soundness, it did not yield a single test bar that would go through a period of strictly plastic flow in tension. There were no visible slipbands. And here too the surfaces of all test bars exhibited hairlike cracks and the fractures

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* This bar was supposed to be fully degasified when received by the author. It was discovered later that it was set aside as incorrectly treated and shipped by mistake. Its description is included to show that nothing short of perfect degasification can produce a truly plastic wirebar.

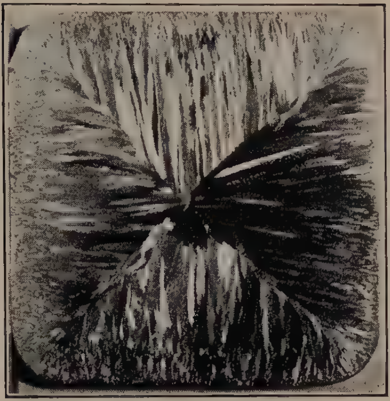
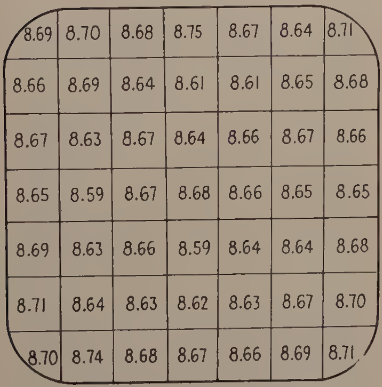
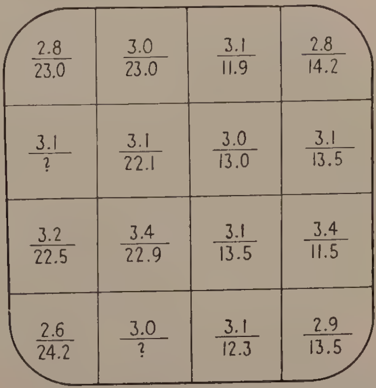


FIG. 7.—MACROSTRUCTURE OF VERTICALLY CAST, INCOMPLETELY DEGASIFIED WIREBAR. AVERAGE DENSITY 8.66.



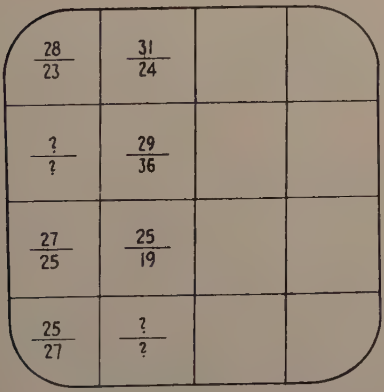
8.69	8.70	8.68	8.75	8.67	8.64	8.71
8.66	8.69	8.64	8.61	8.61	8.65	8.68
8.67	8.63	8.67	8.64	8.66	8.67	8.66
8.65	8.59	8.67	8.68	8.66	8.65	8.65
8.69	8.63	8.66	8.59	8.64	8.64	8.68
8.71	8.64	8.63	8.62	8.63	8.67	8.70
8.70	8.74	8.68	8.67	8.66	8.69	8.71

FIG. 8.—DENSITY DISTRIBUTION OF BAR IN FIG 7.



2.8 23.0	3.0 23.0	3.1 11.9	2.8 14.2
3.1 ?	3.1 22.1	3.0 13.0	3.1 13.5
3.2 22.5	3.4 22.9	3.1 13.5	3.4 11.5
2.6 24.2	3.0 ?	3.1 12.3	2.9 13.5

FIG. 9.—PERCENTAGE OF POROSITY (UPPER VALUES), ULTIMATE TENSILE STRENGTH (LOWER VALUES, LEFT), IZOD (LOWER VALUES, RIGHT) OF BAR IN FIG. 7.



28 23	31 24		
? ?	29 36		
27 25	25 19		
25 27	? ?		

FIG. 10.—ELONGATIONS AND AREA REDUCTIONS (LOWER VALUES) OF BAR IN FIG. 7.

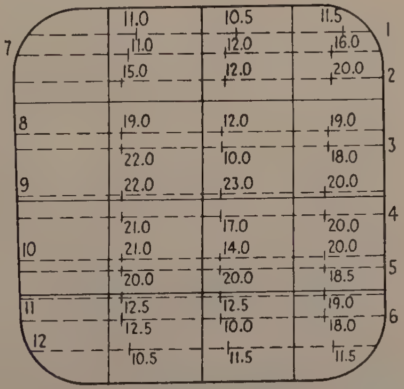


FIG. 11.—DISTRIBUTION OF IMPACT RESISTANCE VALUES IN THE TRANSVERSE DIRECTION OF BAR IN FIG. 7.

contained globular, lustrous holes. However, their average diameter was about 0.05 mm. and never larger than 0.08 mm.

Two transverse cakes were cut out of the bar and 12 impact-test bars were machined out of them. Each was fractured at three notches, which fell into different macrostructural fields of the cakes (Fig. 10).

TABLE 4.—*Mechanical Characteristics of Vertically Cast Imperfectly Deoxidized Wirebar*

BULK DENSITY 8.66

Location of Bar	Mark	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction in Area, Per Cent	Izod Strength
Corner	7-1	23,000	28	23	
Corner	7-7	24,200	31	27	
Corner	7-01				14.2
Corner	7-16				13.5
Center of surface	7-2	23,000	31	24	
Center of surface	7-5	22,500	27	25	
Center of surface	7-9				11.9
Center of surface	7-12				13.4
Center of surface	7-14				11.5
Center of surface	7-15				12.3
Center of bar	7-4	22,100	29	36	
Center of bar	7-6	22,900	25	19	
Center of bar	7-11				13.0
Center of bar	7-13				13.4

An interesting feature can be derived from these impact tests. Whenever a notch cut across the columnar grain, a high impact strength, varying between 18 and 22 ft-lb. and averaging 21 ft-lb., was recorded. A notch running *through the center* of the cake yielded the highest figure, 23 ft-lb. On the contrary, whenever the notch ran parallel to the direction of the columnar grains, considerably lower values resulted. At points where this parallelism was complete, the impact resistance fell to the average of 11.5 ft-lb. and in spots dropped to 10.5. Close to diagonals the impact values were somewhat higher, running up to 14 and even 17 ft-lb. Fractures showing over 18 ft-lb. stopped without breaking the specimen. All others were clean breaks.

This feature has a strong bearing upon the actual distribution of porosity. Where the fracture had to go through the grains, the pores acted as a mere reduction of the active area. Thus high impact data resulted. It is obvious, however, that the space occupied by the pores along the grain boundaries has a total sectional area that occupies a much larger part of the total boundary surface than would correspond to the porosity percentage. So the grain boundaries are weakened and an intergranular slip-fracture results, owing to a low dynamic resistance.

An Oxygen-free and Gas-free Wirebar

A 4-in. bar was cut into four chunks of 6 in. each to obtain tensile-test bars with vertical axes (16 to a chunk) and three intermediate cakes for transverse test bars (four to a cake). A subdivision of a cake into 49 sections for the determination of specific densities was not undertaken. The samples for this work were obtained from the heads of the tensile bars cut off before testing. Not all had to be used, because it soon became clear that the specific densities ran consecutively above 8.90, sometimes approaching 8.93 and only once as low as 8.87. In other words, there is usually less than 0.45 per cent porosity and frequently it does not go beyond 0.15 per cent. A conclusion can be drawn as a matter of hypothesis that oxygen-free and gas-free copper is close to perfect freedom from such gas as might be present as a separate phase. If any gas remains it is probably occluded in the crystals. The other alternative—that the oxygen-free, gas-free wirebar is absolutely free from intercrystalline shrinkage—is much less probable.

The macrostructure of oxygen-free, gas-free wirebar is shown in Fig. 12. It consists of strictly columnar grains so well defined in their outlines that a doubt might arise as to whether they could be in a close enough contact. At any rate, such a structure would not be good news to a metallurgist bound over to the "fine grain" theory.

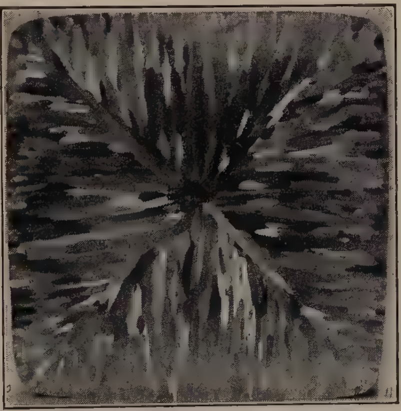


Fig. 12.—Macrostructure of vertically cast wirebar of average density of 8.92.

We shall consider first the characteristics of the metal in the transverse direction. One might expect that far-reaching variations would take place, because each test bar included variable portions of coaxial columnar crystals, transverse columnar grains, diagonal intersections of the two and at least small parts of the large equiaxed grains of the core. Also, since the prevailing opinion is that the diagonals in a casting *must* represent spots of localized weakness, failures might have been expected exactly at such spots.

But contrary to all expectations, the characteristics were amazingly uniform. The six bars taken close to the two opposite surfaces averaged 23,200 lb. per sq. in. tensile strength and the maximum deviation was minus 800 lb. per sq. in., or 3.5 per cent. Average elongation was 47 per cent, with deviations of 2 per cent.

The six inner bars averaged 21,900 lb. per sq. in. strength and 45 per cent elongation, with a maximum variation of 400 lb. per sq. in., or less

TABLE 5.—*Characteristics in Transverse Direction of Vertically Cast Wirebar of Oxygen-free, Gas-free Copper*

BULK DENSITY 8.91

Location of Bar	Mark	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction in Area, Per Cent
Outer quarters	2-1	23,000	46	70
Outer quarters	4-1	23,800	49	72
Outer quarters	5-1	23,300	46	59
Outer quarters	2-4	23,300	46	71
Outer quarters	4-4	23,400	47	84
Outer quarters	5-4	22,400	48	72
	Average	23,200	47	71
Inner quarters	2-2	21,600	48	82
Inner quarters	4-2	21,900	45	86
Inner quarters	5-2	21,800	45	82
Inner quarters	2-3	21,500	46	76
Inner quarters	4-3	22,300	41	85
Inner quarters	5-3	22,300	46	68
	Average	21,900	45	80

than 2 per cent in the first and 4 per cent in the second. And had each layer been considered separately, the agreement would have been even more remarkable. Look at the figures of 23,000, 23,800 and 23,300 lb. per sq. in. strength in the bars identified by the mark 1 (surface quarters taken along the same surface).

Further, not a single bar failed in a region that corresponded to the diagonals. Some fractures occurred at points where the grains were broken across; most test bars failed close to their center in the region where intergranular fractures might have been expected.

Every bar out of the 12 tested went through a long period of plastic flow before failing; a strong neck formation took place, preceded by the formation of numerous slipbands at almost equal distances from one another.

Area reductions could not be computed with enough precision. The fractures had most diversified outlines and the tendency to form some modification of the cup and cone fracture common to all fine-grained and thoroughly worked metals was apparent. It can be stated that in no case was the area reduction lower than 60 per cent, while sometimes it went definitely above 80 per cent.

Of the 64 pieces intended for the axial test bars only 35 were finished after a center rest was used. Others were ruined by being heavily bent and twisted in machining. Taking first the nine bars representing the corner quarters, we find an average tensile strength of 24,400 lb. per sq. in.

TABLE 6.—*Characteristics in Axial Direction, Same Bar as in Table 5*

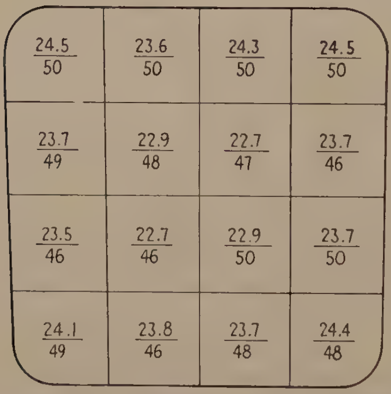
Density	Location	Mark	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
	Corners....................	3-1	24,500	46	72
8.91		6-1	24,500	55	63
8.92		1-7	24,300	48	73
		3-7	23,500	49	72
8.91		6-7	24,400	50	63
		1-01	24,400	51	59
8.88		6-01	24,600	50	65
		1-16	24,400	52	82
8.89		6-16	24,400	45	55
		Average	24,400	49.5	67
	Inner parts of surfaces.......	3-2	23,500	46	70
8.92		6-2	23,800	55	74
		1-3	23,700	43	82
8.90		3-3	23,500	51	68
8.92		6-3	24,000	43	59
		3-5	23,200	52	72
8.93		6-5	23,700	40	59
		1-8	23,500	43	70
8.90		3-8	23,900	46	70
8.91		6-8	24,100	47	72
		1-9	24,500	50	78
8.92		6-9	24,000	50	68
8.91		6-12	23,700	46	78
		1-14	23,500	51	84
8.91		6-14	24,000	49	70
8.87		1-15	23,800	50	61
8.87		6-15	23,600	46	72
		Average	23,800	47.5	71
8.89	Center of bar..............	1-4	23,100	48	74
		3-4	22,700	45	74
8.92		6-4	23,000	52	68
		1-6	23,300	45	77
		3-6	23,100	46	70
8.93		6-6	21,800	46	63
		1-11	22,700	45	68
8.91		6-11	22,800	50	68
8.90		6-13	22,900	50	76
		Average	22,800	47	70

and an average elongation of 49.5 per cent; maximum deviation: minus 900 lb. per sq. in. (3.7 per cent) and minus 4.5 per cent (9 per cent) in elongation. And there were *six* bars among the nine with a tensile strength between 24,400 and 24,500 lb. per sq. in. A variation less than 0.5 per cent!

Taking the 17 bars corresponding to the eight quarters next to the centers of the side surfaces we find an average strength of 23,800 lb. per sq. in. and an average elongation of 47.5 per cent. Both figures are but slightly lower than the characteristics of the corner quarters. The maximum deviations were 800 lb. per sq. in. (3.3 per cent) in strength and 7.5 per cent (16 per cent) in elongation. And there were *ten bars* with tensile strength between 23,600 and 24,000 lb. per sq. in.; i.e., not deviating over 1 per cent from the average.

Finally, for the four inner quarters, represented by 9 bars, we find 22,800 lb. per sq. in. average tensile strength and 47 per cent elongation, with maximum deviations of 1000 lb. per sq. in. (4.4 per cent) and 5 per cent (10.5 per cent). *Five* values were included within 22,700 and 22,900 lb. per sq. in.; i.e., did not deviate by a full 1 per cent of the average.

All of the 35 bars developed necks before failing and only one exhibited a single *intergranular* fracture on its surface. The distribution of tensile strengths and elongations is shown in Fig. 13.



24.5 50	23.6 50	24.3 50	24.5 50
23.7 49	22.9 48	22.7 47	23.7 46
23.5 46	22.7 46	22.9 50	23.7 50
24.1 49	23.8 46	23.7 48	24.4 48

FIG. 13.—DISTRIBUTION OF ULTIMATE TENSILE STRENGTH (1000 LB. PER SQ. IN.) AND PERCENTAGE OF ELONGATION THROUGH CROSS SECTION OF VERTICALLY CAST OXYGEN-FREE, GAS-FREE COPPER WIREBAR OF AVERAGE DENSITY OF 8.92.

Let us imagine now an idealized wirebar (Fig. 14) with a perfectly uniform gradient of mechanical characteristics from the center to the surface. In such a bar, as the first approximation, there will be four central quarters with an average tensile strength of 22,800 lb. per sq. in. and an elongation of 47 per cent; eight surface quarters with a strength of 23,800 lb. per sq. in. and an elongation of 47.5 per cent; four corner quarters with a tensile strength of 24,400 lb. per sq. in. and an elongation of 49.5 per cent.

Again, supposing the gradient to be constant, we may compute the following possible distribution of tensile strengths and elongations: surface layer at the corners (rounded) 24,800 lb. per sq. in., 50 per cent elongation; surface layer at centers of surfaces, 24,000 lb. per sq. in. and 48 per cent elongation; central core, 22,000 lb. per sq. in. and 46.5 per cent elongation.

This goes to show that the idealized bar, differing from the real one merely in the perfect symmetry of its distribution of characteristics, would represent a nearly perfect body of constant properties differing but little from the surface to the center.

Far more striking in comparison to the impact characteristics of the tough-pitch bar and the bar of density 8.66 are the Izod values of the oxygen-free, gas-free wirebar. To obtain these a chunk taken from a wirebar was divided into 49 square rods running parallel to the axis of the

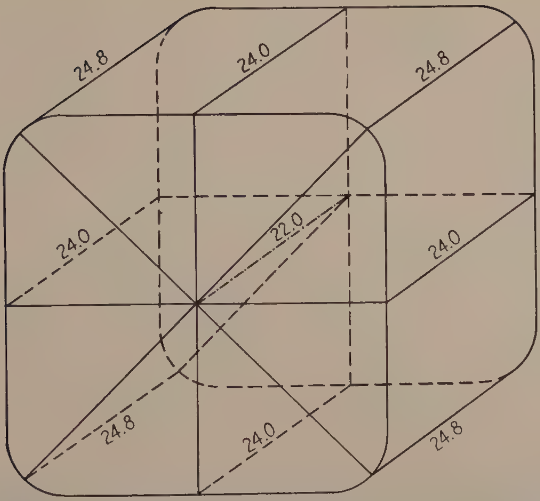


Fig. 14.—Distribution of tensile strength in idealized oxygen-free, gas-free wirebar of 8.91 bulk density.

bar. The odd numbered pieces were used for impact tests, and from the core of the bar three even numbered test pieces were used in addition. The data so obtained are averages from three and sometimes four figures. They are shown in Fig. 15. Only two bars out of 28 showed an Izod value as low as 25.5. Five bars had the maximum value of 31.0 or slightly better. The average figure was about 29; near the core it averaged 27.5.

These figures prove that a blow struck perpendicular to the axial direction does not tend to separate the grains but merely deforms them. In fact, of all the 28 pieces tested not a single one approached a break at any of its notches. Only the superficial layer opened and that not more than 0.02 in. deep. Taking into consideration the fact that the absorption of dynamic energy in an impact test resulting in a pure deformation must depend upon the incidental volume of the grains participating in the deformation, the agreement between the values observed is strikingly close.

30		28		31		30
	30		31		31.5	
31		28		29.5		28.5
	25.5	25.5	28	27	30	
31		27.5	28.5	27		26
	30		28		27.5	
27.5		28.5		31.5		29

Fig. 15.—Distribution of Izod impact values through cross section of oxygen-free, gas-free copper wirebar.

But how would the test pieces taken in the transverse direction behave? In Fig. 11 a good wirebar of an average density of 8.66 shows values of 20 Izod or over where the notch crosses the columnar grains but as low as 10 where it runs parallel to them. This question was answered by testing 14 impact bars cut out of two cakes ½ in. thick, taken from different points in the original wirebar. The results are shown in Figs. 16 and 17. Each of the 14 bars was tested at three notches. In none of the 42 tests did a bar break or even open up more than to the depth of 0.02 in. The lowest Izod value for one of the cakes was 25, for the second 23; the

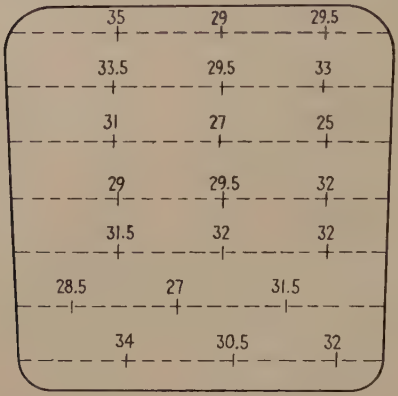


Fig. 16.

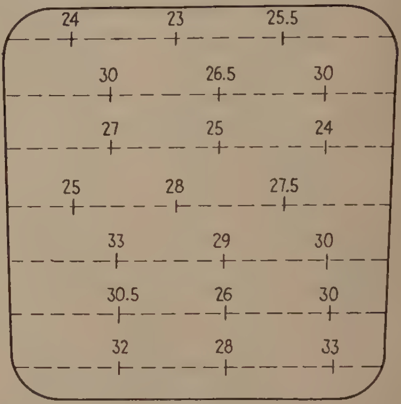


Fig. 17.

Fig. 16.—Transverse Izod impact values in a slice of oxygen-free, gas-free copper wirebar of average density 8.92.

Fig. 17.—Transverse Izod impact values in another slice of same wirebar as in Fig. 16.

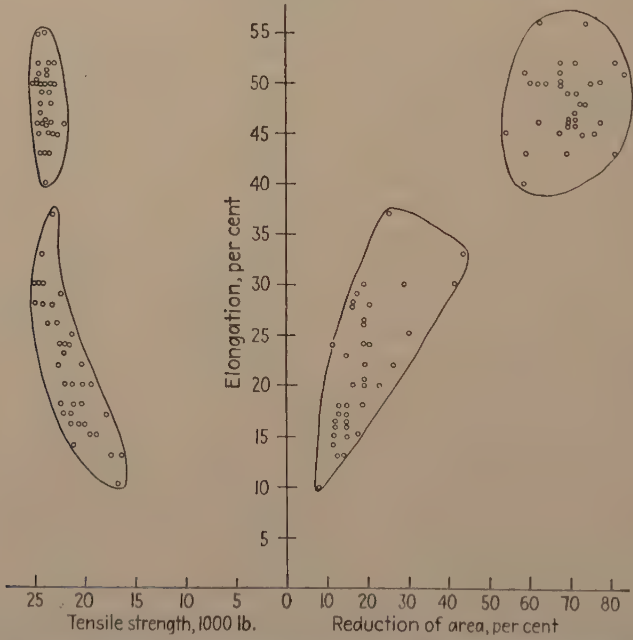


Fig. 18.—Relationship between elongation, tensile strength and reduction in area in horizontal tough-pitch and vertical oxygen-free and gas-free wirebars.

maximum was 34 in the first, 33 in the second; averages, 31 in the first, 28 in the second.

These figures demonstrate again the high characteristics of the oxygen-free, gas-free wirebar. No matter what direction is chosen, the impact values remain high. No impact separates the grains; it deforms

TABLE 7.—*Comparison of Bars*

	TOUGH-PITCH BAR	OXYGEN-FREE, GAS-FREE BAR
Bulk density	8.35–8.50	8.91
Local density variations	8.75 at bottom corners 8.30 in weakest spots	8.88–8.93 located at random
Tensile strengths, lb. per sq. in.	About 25,000 at bottom corners, probably due to spontaneous hardening by precipitated copper monoxide; about 17,000 at weakest spot	About 24,800 in surface layer of corners. Not less than 22,000 in center of bar
Elongations, per cent in 2 in.	About 31 average maximum; incidentally 37 maximum About 13 average minimum, incidentally as low as 10	Nowhere less than 40, mostly above 47; incidentally up to 55
Area reductions, per cent	Average maximum 27; incidentally 42 Average minimum 13; incidentally 8	Nowhere less than 60; average about 70; incidentally over 80
Impact resistance	Average value not over 10 Izod. A few spots may show 15; many 8.5. Most tests result in clear breaks. Incomplete fractures rare	Average value about 29 Izod; in spots as high as 33. Never drops below 23. All tests end in a pure bend, no spot opening up by more than 0.02 in. in depth
Qualitative observations	Fractures abrupt, not a trace of plastic flow; no neck formation. Many incipient surface cracks. Fractures mostly intergranular. Fractures show pinholes due to gas. Fractures ragged but run close to horizontal plane. No slip plane and no cup and cone formation noticed. Broken tensile bars have a lowered density even for test bars taken from densest spots	Always forms a neck. Develops uniformly running slip bands. Pure plastic flow clearly observable. Few surface cracks observable. Fractures strictly intragranular. Fractures show a few sharp holes where part of a grain was pulled out. No visible gas holes. Fractures rather various in shape, owing to size of grains and their high plasticity. Tendency to cup and cone formation visible; in its absence, definite slip plane forms. No lowering in density noted in broken bars beyond 0.03, which may be incidental. Most samples retained full density

them and might crack them if the limits of stress were passed but the fracture would have no tendency to run along the boundaries. There is no weakness whatsoever attached to the latter.

CONCLUSIONS

And so we come to see that out of three wirebars the one with the largest grains showed the highest mechanical characteristics all over and in any direction. The writer reiterates his deep conviction that the fineness of grain has nothing to do with the quality of a metal. Quality depends exclusively on the purity of a metal or alloy, especially its freedom from gas. Only where gas is present does the fineness of grain become important, because it helps to refine the gas pockets and pores, so making them less extensive in surface and therefore less harmful.

Fig. 18 presents graphically the relationship between elongations, tensile strength and reduction in area in the horizontal tough-pitch and vertical oxygen-free, gas-free wirebars. Two three-dimensional bodies are assumed, every point of which has for its coordinates these three features of the respective wirebars, and the projections of the two bodies on the planes are obtained—elongation-tensile strength and elongation-area reduction. Their positions and shapes show clearly that the characteristic complexes of mechanical features have no common part whatsoever.

ACKNOWLEDGMENTS

The author wishes to express his indebtedness to the U. S. Metals Refining Co. for supplying the large amount of metal used in the course of this investigation. He is indebted also to the Engineering School of the College of the City of New York, in whose laboratories the mechanical tests were made, and to Prof. J. S. Peck, who supervised the testing; to the Andrew Campbell Division of the American Chain and Cable Co., of Bridgeport, Conn., for assistance in the cutting up of the wirebars with its abrasive-wheel cutting machines; to the Burndy Engineering Co., makers of electrical connectors, for numerous favors accorded to him during this investigation.

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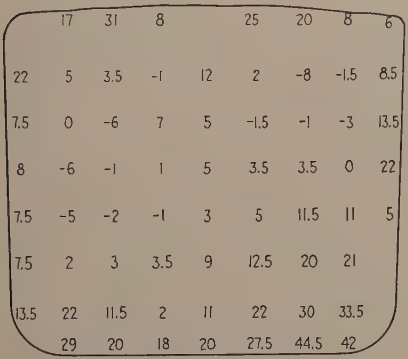
DISCUSSION

(*Jerome Strauss presiding*)

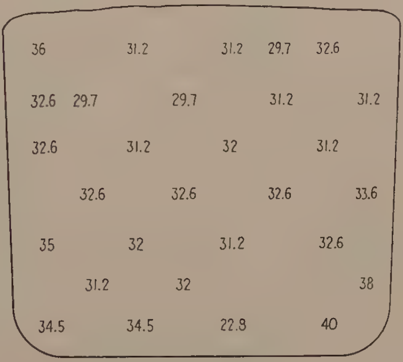
J. S. Peck,* New York, N. Y.—I am not a professional metallurgist, but I happen to have made the mechanical tests for Mr. Corson on which he based his paper. There are some more tests which he did not include, covering the hardness of the two types of copper, which I should like to present to you and show you how I tried to interpret the results by a rather simple statistical technique.

We first started with the Rockwell hardness, the E scale; that is, using an ⅛-in. ball and a 100-kg. load. This is the distribution of the hardness tests over the area of the tough-pitch copper slab that was cut from the ingot (Fig. 19). There is a very high spot (in one corner) and three rather soft spots—one in the center. To interpret such a series of tests is rather difficult without the use of some statistical technique. In studying all these hardnesses, I first determined the mean of all the observations and then the constant, which we call the standard deviation; in other words, the square root of the mean square deviation. For the particular case of Fig. 19, the mean of all those values was 10.3 and the standard deviation was 11.5. That means that 68 per cent of all the tests made fell between the values of 21.8 and minus 1.2, rather a big spread. That seemed to be too great a variation, and in order to determine what was causing it, we made a second run, using the Brinell hardness system.



Rockwell E hardness
⅛-in. ball, 100-kg. load

Fig. 19.



Brinell hardness

Fig 20.

Fig. 20 shows the distributions of the Brinell hardness using a 500-kg. load. Again we found the high spot in the corner, hard, and soft in about the same regions. But now the average of those determinations was 32.3 with a standard deviation of only 3.1, and the spread of the 68 per cent of all the tests was between 35.4 and 29.2. I will summarize these means afterward.

The distribution of the Rockwell hardness over the surface of the oxygen-freed ingot is in Fig. 21. The mean in this case was 28.3 and the standard deviation was 10.2. The spread corresponded closely to the spread obtained in the tough-pitch bar of 11.5. Here 68 per cent of all our values fell between 38.5 and 18.1, again a very high variation in the Rockwell test.

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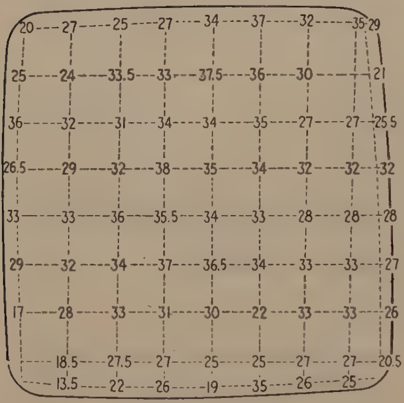
* Professor of Civil Engineering, College of the City of New York.

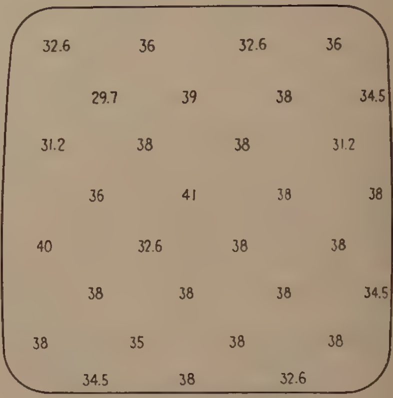
The oxygen-free slab tested with Brinell hardness gave this distribution (Fig. 22), rather uniform over the entire surface. The mean was 36.2 and the spread only 1.9, the standard deviation, giving our values between 38.1 and 34.4 for 68 per cent of the cases. Those were the results of the hardness tests.

For the Rockwell hardness the tough-pitch gave a mean of 10.3 and the oxygen-free of 28.3; with the Brinell, the tough-pitch mean was 32.3 and the oxygen-free 36.2. Now the problem is what significance does the difference of those means have? The difference in this case (Rockwell) is 18, and in this one (Brinell) 3.9. In other words, if we performed this test ten times, would we get differences greater than these, equal to them, or would the differences reverse? Would the one that was low become higher the second time? There is a very simple statistical technique for determining the significance of these means, the difference of the means. We found that if these tests were repeated any number of times, the chances of getting a difference as great as this or greater, owing only to random errors of sampling and random distribution of hardness over the section, was somewhere around one in ten million, which meant that something was causing that difference. There was a true difference there even though it was as small as 3.9. The same argument, of course, holds for the touch-pitch difference of 18. But we found that for the value we will call x/σ the significance of this difference was about 16½ for the Rockwell hardness and in the Brinell hardness somewhere around 57. Those are the sigma positions on a normal distribution curve, so we can say that this 3.9 really is much more significant in measuring the difference of hardness, the average difference of hardness between the two types of copper, than the 18, the larger difference.



Rockwell E hardness
⅛-in. ball, 100-kg. load

FIG. 21.



Brinell hardness

FIG. 22.

It is hard to account for the greater variation given by the Rockwell test unless the Rockwell is a much more sensitive test. Naturally it is, because it uses a ⅛-in. penetrator as against a 10-mm. penetrator in the Brinell. The Brinell impression may break through several crystals and average up their hardness, whereas the Rockwell may pick one individual crystal and give its hardness. That seemed to be the explanation.

In getting a picture of the difference of hardness between the two types of copper, the average difference, the Brinell with this difference of 3.9 in favor of the oxygen-free copper is a much more significant and better value.

S. Rolle,* New York, N. Y. (written discussion).—As producers of OFHC copper, it was perhaps natural for us to realize somewhat earlier than others that OFHC possesses certain toughness not found in ordinary electrolytic copper. The well-known twist test reveals the greater resistance to twisting of wire made from OFHC as compared to that made from ordinary tough-pitch copper (horizontally cast). But, it is rather difficult to carry out this test under uniform conditions; moreover, the work required per twist increases as twisting proceeds, so that the ratio between the work done in twisting OFHC wire and tough-pitch wire is not the same as the ratio between the number of twists. It was, therefore, decided to determine the toughness of the two kinds of copper in fabricated form by making Izod notched-bar tests using a Losenhausen pendulum impact tester.

The specimens for the Izod test were prepared in the following manner: Ordinary horizontal electrolytic tough-pitch copper wirebars and OFHC wirebars were hot-rolled and drawn in a commercial plant to ½ by ½-in. (12.7 by 12.7-mm.) square rod having a hardness in terms of ultimate tensile strength of approximately 47,000 lb. per sq. in. (33 kg. per sq. mm.).

Suitable lengths of the hard rod were machined to 0.406 in. square, and half of the samples of both kinds of copper was annealed in air in an electric furnace at 450° C. for 1 hr. and quenched in water. Final machining was accomplished with very light cuts, making the test specimen 0.3937 ± 0.001 in. (10 mm.) square and 3 in. (76.2 mm.) long. One notch was cut in each of two adjacent sides of each specimen, 1.102 in. (28 mm.) center to center, approximately equidistant from the ends. The notches were 45° ± 1°, 0.0787 in. (2 mm.) deep, with a radius of 0.01 in. (0.25 mm.) at the bottom.

Two tests were made on each specimen, of which there were 15 for each kind of copper in the annealed condition and in the hard-drawn condition. The impact values of the 60 samples tested are shown in Tables 8 and 9. The physical properties and the average impact values shown in these two tables are given in Table 10.

The results obtained clearly indicate that OFHC is tougher than electrolytic tough-pitch in both the annealed and the hard-drawn conditions, and whereas cold-working increases the resistance to impact of OFHC, the reverse is true of the other.

Many investigators have reported similar results but, as far as the writer knows, no one has offered a plausible explanation of this characteristic until Mr. Corson called attention to the marked differences in the physical characteristics of the two kinds of copper in cast form. For the tough-pitch bars, he found that even when the bulk density was high; there were areas in most, if not all, bars which were statically weak; these areas corresponding to the areas having high porosity. Stress applied to such bars causes rupture before much plastic flow takes place.

On the other hand, the OFHC bars, being of high density throughout, were found to be statically strong. The columnar grains are in close contact with one another and applied stress causes considerable plastic flow before rupture takes place.

D. K. Crampton,† Waterbury, Conn.—I represent a very large consumer of copper in various forms, not a producer, and I hold no brief for any particular kind of copper. Speaking from the technological standpoint, the data presented in this paper, and similar data that have been shown before, are most interesting and are facts to be taken pretty much at face value.

There are at present at least two procedures being used for production of copper of the general quality described here, and there are others in process of development, which perhaps before long will be available. I am strongly in favor of any procedure that will tend to give a higher quality and more uniform product.

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* United States Metals Refining Co.

† Director of Research, Chase Brass and Copper Co.

TABLE 8.—*Log of Test, OFHC Copper*

Annealed		Hard-drawn	
Sample No.	Impact Strength, Ft-lb.	Sample No.	Impact Strength, Ft-lb.
U-1	53	V-1	73
U-2	54	V-2	75
U-3	55	V-3	73
U-4	55	V-4	70
U-5	54	V-5	67
U-6	53	V-6	72
U-7	54	V-7	72
U-8	54	V-8	73
U-9	55	V-9	75
U-10	54	V-10	75
U-11	53	V-11	74
U-12	54	V-12	77
U-13	55	V-13	72
U-14	54	V-14	75
U-15	54	V-15	74
Average............	54.1	Average...........	73.2

TABLE 9.—*Log of Test, Tough-pitch Copper*

Annealed		Hard-drawn	
Sample No.	Impact Strength, Ft-lb.	Sample No.	Impact Strength, Ft-lb.
W-1	48	X-1	36
W-2	50	X-2	36
W-3	50	X-3	36
W-4	48	X-4	37
W-5	50	X-5	35
W-6	49	X-6	35
W-7	47	X-7	35
W-8	48	X-8	36
W-9	50	X-9	38
W-10	49	X-10	36
W-11	48	X-11	36
W-12	48	X-12	32
W-13	47	X-13	36
W-14	48	X-14	32
W-15	47	X-15	35
Average............	48.5	Average...........	35.4

We should consider the application to which the copper is to be put. There are certain uses where even the relatively smaller differences that still exist after fabrication are highly important. Resistance to hydrogen embrittlement, for instance, and the effect of minor physical discontinuities that still exist are of paramount importance for certain applications, and in those uses there can be no question but that the oxygen-free types of copper are advantageous. There are other uses for copper where such differences as still exist after fabrication are of relatively less importance, or perhaps of no importance, and for such uses naturally the one product is as good as the other.

TABLE 10.—*Average Impact Values*

Material	Brinell Hardness	Tensile Strength, Lb. per Sq. In.		Reduction of Area, Per Cent	Elongation, Per Cent		Impact, Ft-lb.
		2 In.	8 In.		2 In.	8 In.	
OFHC:							
Annealed	50	32,380	31,000	92	52.5	43.5	54.1
Hard-drawn	92	46,890	46,250	89	21.5	5.0	73.2
Electrolytic tough-pitch:							
Annealed	54	32,565	31,000	73	54.0	43.5	48.5
Hard-drawn	91	48,400	47,500	57	15.5	4.0	35.4

Considered from the economic standpoint, which perhaps in the last analysis determines many of these questions, I am going to make a rather trite remark, that the product is worth what you can get for it. We all know that if we are producers of copper or copper alloys or of steel or whatnot and go to a prospective consumer of our products to offer some new modification that shows certain technological advantages, he always evinces interest and he is strongly inclined toward the new product. However, when we tell him what it costs, he may still retain that interest or he may lose considerable of it. The point I want to make is that for certain uses the advantages of oxygen-free types of copper are worth anything that they cost, and my prediction is that there will be an increased use of that type of copper in certain fields. In other fields of use, oxygen-free types of copper will increase but perhaps less rapidly, the reason being that advantages are perhaps less obvious. I believe there are other fairly large fields where the actual dollars and cents value of such technological advantages as appear are not worth anything at all and people will not pay anything to get them.

I think, in spite of all I have just said, that the work that Mr. Corson has done is most interesting and I should like to see further such material published. Users of copper cannot help but feel that it is very much worth while.

W. H. BASSETT, JR.,* Hastings-on-Hudson, N. Y. (written discussion).—Mr. Corson's work has compared the density characteristics, tensile strength, elongation, and impact strength of various wirebars in the cast condition. The user of copper wirebars is more interested in the ultimate physical properties of the wirebars after they have received the normalizing and homogenizing treatment resulting from the heat-treating and working of the metal during rolling and drawing operations. Our studies have indicated that the density is brought to a normal uniform value, the normal porosity being eliminated, when the metal is homogenized by the heat-treating and working operations, which give it the more uniform structure and physical properties.

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* Manager, Metallurgical Development, Anaconda Wire and Cable Co.

We obtained eight small copper bars approximately 1 in. square and 42 in. long, by cutting a standard 300-lb. wirebar as shown in Fig. 23. One-half inch was milled off the bottom of the wirebar before the bottom was cut lengthwise, so that the bottom sections represented copper from the best part of the wirebar. The top sections included the crinkly top surface of the wirebar as one side.

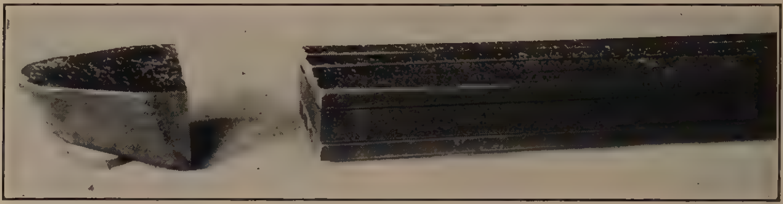
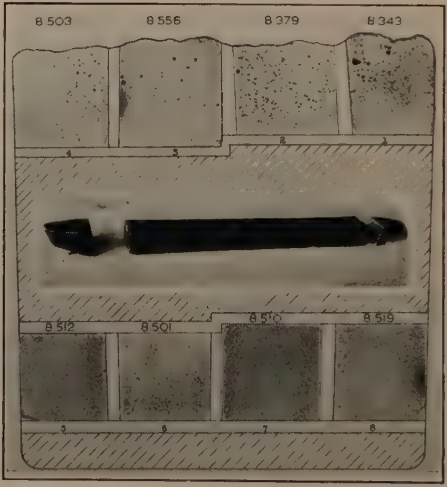


FIG. 23.—METHOD OF CUTTING WIREBAR.



Top Section	Density	Bottom Section	Density
1	8.343	5	8.512
2	8.379	6	8.501
3	8.556	7	8.510
4	8.503	8	8.519
Average....	8.447	Average....	8.511

FIG. 24.—METHOD OF CUTTING WIREBAR TO SHOW EFFECT OF "SET" SURFACE.
Density and porosity of eight 1-inch square sections.
Average density of sections 1 to 4.......................... 8.447
Average density of sections 5 to 8.......................... 8.511

Our method of sectioning the wirebar is again shown diagrammatically in Fig. 24, together with the porosity of each 1-in. square section of the wirebar. One-inch cubes were carefully polished and weighed for specific density; the results of which are shown on Fig. 24 and in the table below it.

The density of the four top sections averaged 8.447 against an average of 8.511 for the bottom section, which closely approximates the figures reported by Mr. Corson in Fig. 2.

The porosity of each of the eight 1-in. square sections, after a microscopic polish, is shown at a magnification of approximately two times by photographs in Fig. 24. We made no attempt to evaluate porosity in per cent but it is plainly shown that fine pores were present all through the wirebar together with larger holes near the top surface where the density was lowest. Section 3 in the top showed the least porosity and had the comparatively high density of 8.556.

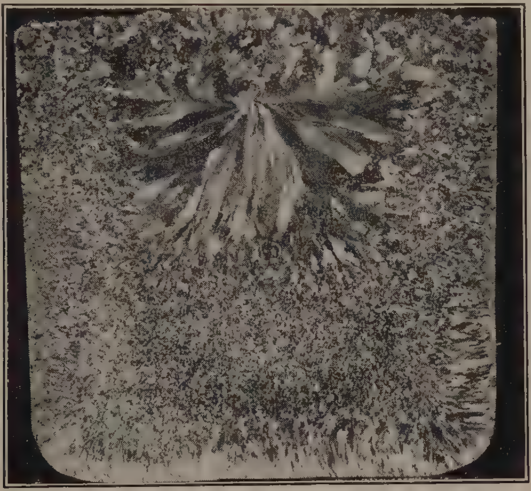


Fig. 25.—Macrostructure of wirebar.

The general grain structure of the wirebar used for test is shown in Fig. 25. The macrostructure of the eight 1-in. square sections, photographed at a magnification of approximately two diameters, is shown in Fig. 26. The four bottom sections were made up entirely of uniform small grains. The top sections showed large-grained dendritic structures with a thick layer of oxygen-rich eutectic at the top surface.

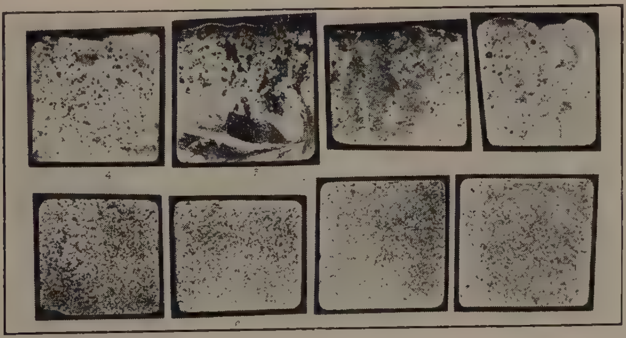


Fig. 26.—Macrostructure of eight 1-inch square sections.

Fig. 27 shows the typical dendritic cast structure near the top edge of section 2. The dark, speckled areas are oxygen-rich. Fig. 28 shows the structure near the lower edge of section 2 and the presence of an appreciable amount of oxygen-rich constituents is evident at the grain boundaries at this location 1 in. below the surface of the wirebar. The structure of the bottom four sections contained a comparatively small amount of oxygen-rich constituent (Fig. 29). The eight 1-in. square 42-in. long bars were hot-rolled to $\frac{5}{16}$-in. dia. rods with 10 passes and cold-drawn to 0.104-in. dia. hard wire in a standard continuous wire-drawing machine.

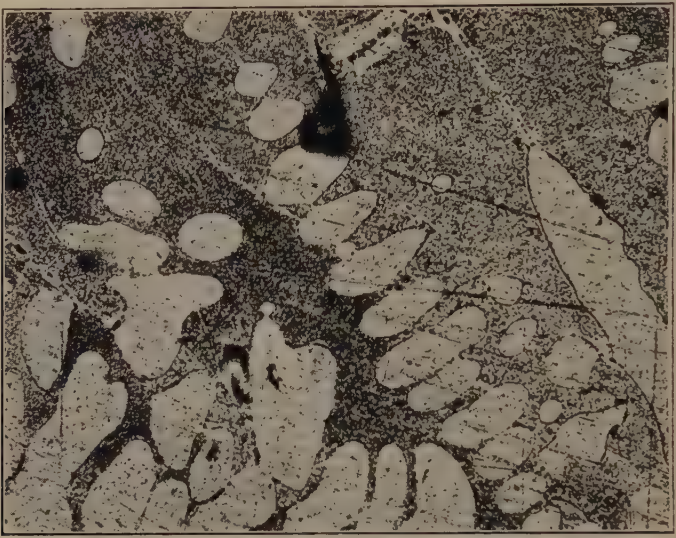


FIG. 27.—MICROSTRUCTURE NEAR TOP EDGE OF WIREBAR. × 100.

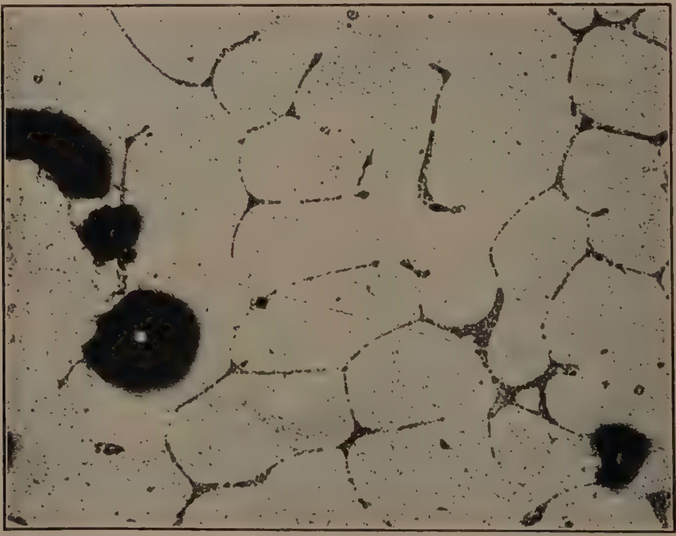


FIG. 28.—MICROSTRUCTURE 1 INCH BELOW TOP OF WIREBAR. × 100.

Density tests on the eight $\frac{5}{16}$-in. dia. hot-rolled rods showed that the heating and working of the metal had increased the specific density from the values previously shown for the 1-in. square cast sections. The heating and rolling of the copper had eliminated the porosity and increased the specific density to a value normal for fabricated tough-pitch copper (Table 11).

TABLE 11.—*Tests on $\frac{5}{16}$-in. Rods*

Top Section	Density	Bottom Section	Density
1	8.903	5	8.928
2	8.905	6	8.927
3	8.912	7	8.926
4	8.911	8	8.925
Average..........	8.908	Average.........	8.926

The average density of rod from the four top sections of the wirebar was 8.908 and of rods from the four bottom sections, 8.926. The spread in density between the top and bottom sections of the wirebar had therefore been reduced from 0.064 for the cast samples to 0.018 for the fabricated samples. This final difference of 0.018 is attributed to a difference in oxygen content.

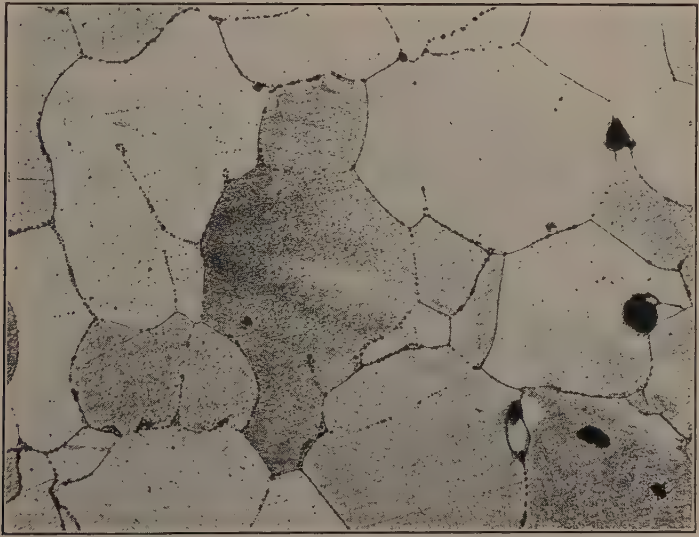


FIG. 29.—MICROSTRUCTURE NEAR BOTTOM OF WIREBAR. × 100.

Tests on the hot-rolled rods showed a consistent difference in the composition and electrical properties of the two groups of copper rods (Table 12). This table shows the results of assaying the eight rods. The top group, Nos. 1 to 4, averaged 99.947 per cent copper + silver, as against an average of 99.963 per cent for the bottom group, Nos. 5 to 8, indicating an average excess of 0.016 per cent oxygen in the top sections. This difference in composition produced a difference of 0.50 per cent in the electrical conductivity of the copper.

The structure of the $\frac{5}{16}$-in. dia. rods from the four top sections retained the oxygen-rich area from the "set" surface of the wirebar, as shown by the dark edge on each of the macrographs in Fig. 30. The oxide concentration in the edge of these rods occupied nearly $\frac{1}{4}$ of their circumference and about $\frac{1}{3}$ of the diameter of rods 2 and 3, because these were fabricated from only the top section of the wirebar. In contrast with the previous structures are those of rods 5 to 8, which were found to have a uniform grain structure throughout their entire area, owing to the use of only the bottom section of the wirebar during fabrication (Fig. 31).

TABLE 12.—*Composition and Electrical Properties*

Section	Copper + Silver, Per Cent	Conductivity International Annealed Copper Standard at 20° C, Per Cent	Density
1	99.954	100.71	8.903
2	99.940	100.77	8.905
3	99.952	100.57	8.912
4	99.942	100.87	8.911
Average 1 to 4....	99.947	100.73	8.908
5	99.962	101.20	8.928
6	99.966	101.22	8.927
7	99.960	101.21	8.926
8	99.962	101.29	8.925
Average 5 to 8....	99.963	101.23	8.926

The structure at the set edge of rod No. 2, magnified 100 diameters, is shown in Fig. 32. Of course this dense oxide concentration is about five times greater than would be obtained in a normal copper rod because ¼ of the set surface of the wirebar was confined to $\frac{1}{20}$ of the volume of the wirebar. No trace of porosity could be detected in any of the rods. The opposite edge of this rod had a normal structure. The structures shown in these two photomicrographs (Figs. 32 and 33) were typical of rods 1 to 4 from the top of the wirebar.

TABLE 13.—*Effect of Structural Irregularities*

Wire No.	Diameter, In.	Breaking Load, Lb.	Tensile Strength, Lb. per Sq. In.	Elongation in 60 In., Per Cent
1	0.1040	600	70,600	0.96
3	0.1040	584	68,700	0.62
4	0.1040	590	69,400	0.96
Average................	......	591	69,550	0.85
5	0.1040	592	69,700	1.17
7	0.1040	592	69,700	1.25
8	0.1040	588	69,200	1.21
Average................	......	591	69,550	1.21
A.S.T.M. requirements..	0.104	551	64,800	1.00

The edges of the four hot-rolled rods from the bottom of the wirebar were free from oxide concentrations, as shown in Fig. 34, typical of the group.

The structure of wire from the eight rods was, in general, similar to that of their respective rods.

The chief effect of the structural irregularities such as shown on the physical properties of hard-drawn wire was to lower the ductility and toughness of the wire (Table 13). This table lists the breaking strength, tensile strength, and elongation of the eight wires, together with the requirements of the American Society for Testing Materials for 0.104-in. dia. hard wire. The strength of 69,550 lb. per sq. in. for the two groups of wires was similar and well above the A.S.T.M. requirements. Elongation in 60 in. for wires 1, 3 and 4 from the top of the wirebar averaged only 0.85 per cent and failed to meet the A.S.T.M. requirements. The bottom group of wires stretched 1.21 per cent and was satisfactory.

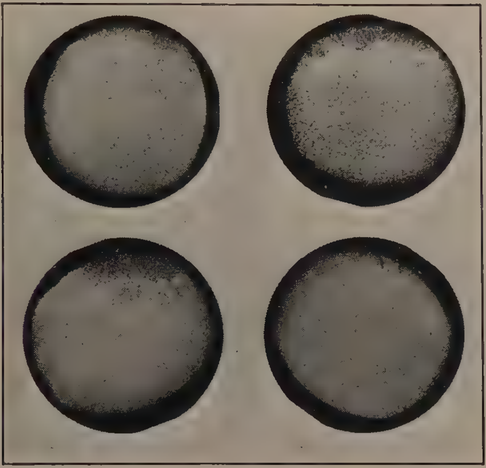


FIG. 30.—STRUCTURE OF RODS (1 TO 4) FROM TOP OF WIREBAR. × 10.

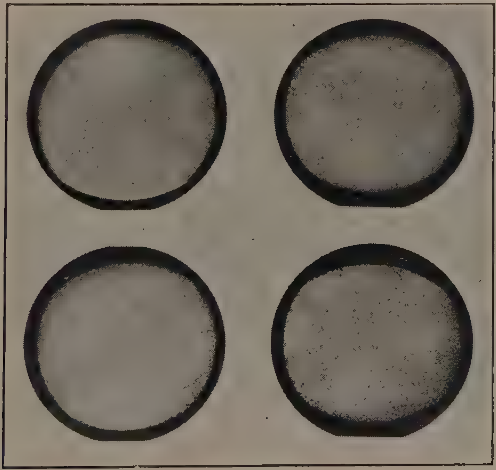


FIG. 31.—STRUCTURE OF RODS (5 TO 8) FROM BOTTOM OF WIREBAR. × 10.

Our data therefore indicate that copper wire containing a dense oxygen concentration in one edge will be satisfactory for service as an electrical conductor except where

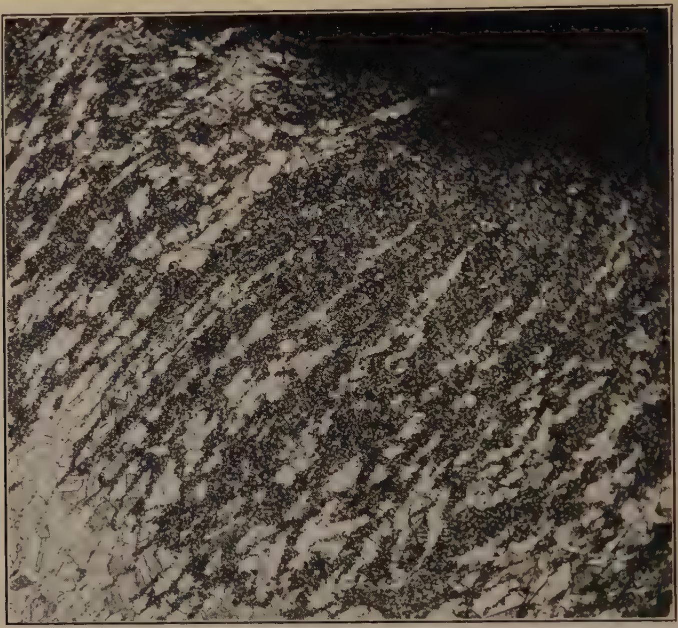


FIG. 32.—STRUCTURE OF EDGE OF ROD NO. 2 CORRESPONDING TO TOP OF WIREBAR. × 100.

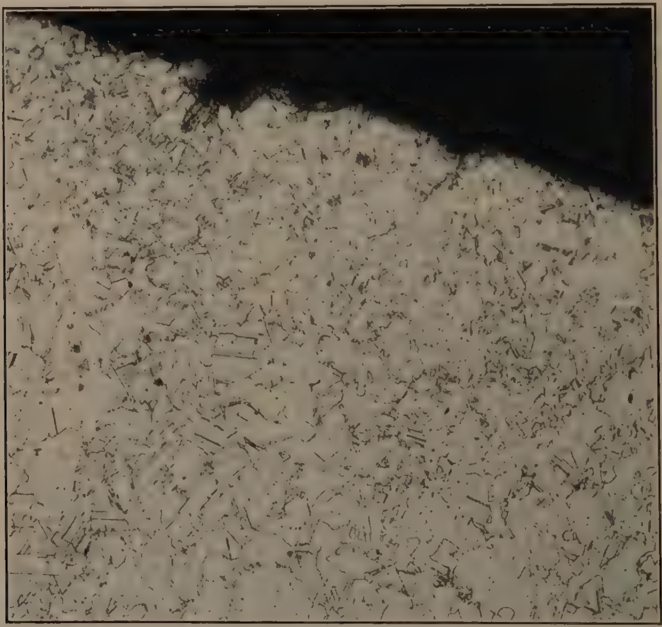


FIG. 33.—STRUCTURE OF OPPOSITE EDGE OF ROD NO. 2. × 10.

unusual ductility is needed. Applications where severe bending or stretching is required should specify wire made from scalped or end-poured wirebars.

Fig. 34.—Typical structure of edges of rods 5 to 8. × 100.

M. G. Corson (written discussion).—I am glad that Professor Peck supplied the data on the hardness distribution through the cross sections of the two types of wirebars described. Of course they are not sufficient to serve as a base for a true "large number" analysis of hardness values, which would require at least 500 to 1000 observations. However, it is not beyond reason to try to produce frequency curves for hardness values without attempting too much fact-fitting. That is exactly what I am going to present here, basing my percentage figures upon a broad examination of Professor Peck's data.

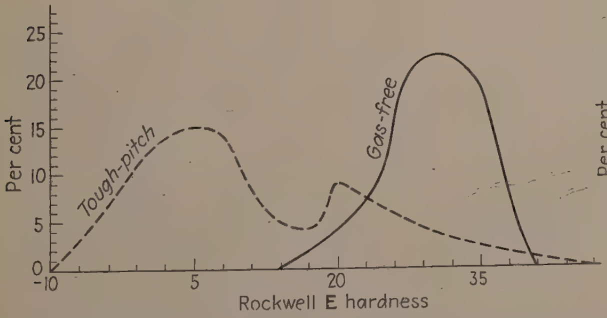


Fig. 35.

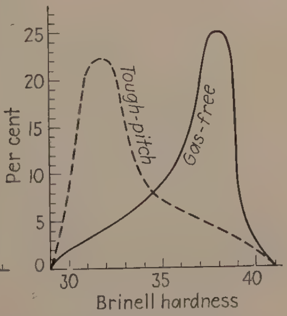


Fig. 36.

Fig. 35.—Frequency of Rockwell E values in tough- pitch and gas-free copper.
Fig. 36.—Frequency of Brinell $^{500}/_{10}$ values in tough-pitch and gas-free copper.

In Fig. 35 the dotted line represents the distribution of Rockwell E values in tough-pitch copper. It is a two-maxima curve starting at minus 10 and ending at 39.

At its left end is the 0 frequency at minus 10 Rockwell, which must correspond to the maximum local porosity. From that point on the curve rises steeply, the maximum frequency corresponding to the hardness of 5 Rockwell induced by some most frequent combination of inherent hardness and porosity. Then the curve drops to a minimum frequency at 19 Rockwell. This minimum can be explained by the comparative rarity of such spots, where porosity is nearly absent and no additional factor interferes.

The second maximum corresponds, probably, to the most frequent combination of intrinsic hardness, minimum porosity and a small amount of extra hardening due to cuprous oxide precipitation. This extra hardening occurs with an ever increasing rarity and spots in which the hardness so induced goes beyond 39 Rockwell are nonexistent (zero frequency).

In gas-free copper, the minimum Rockwell hardness starts with the value of 8. This corresponds evidently to its maximum local porosity which incidentally is matched by the minimum local porosity in tough-pitch copper. The maximum frequency in gas-free copper corresponds to 31 Rockwell, a value that appears with the frequency of 22 per cent. Fully 63 per cent of observations fall between 27 and 35 Rockwell.

Higher values of hardness again become rare, evidently because there is little chance for an extra hardening by cuprous oxide precipitation, owing to the low oxygen content.

Brinell values are not as sensitive, because a much larger volume of the metal becomes affected. Both types of copper wirebars show the presence of Brinell values between 29 and 41; in other words, the same factors—intrinsic hardness, porosity and oxide-hardening—appear in both. However, the most frequent combination of intrinsic hardness and porosity leads to the maximum of 22 per cent of observations at 32 Brinell in tough-pitch copper, while the maximum frequency of 25 per cent corresponds to the value of 38 Brinell in gas-free copper.

Dr. Crampton's statement of the manufacturer's position in relation to the customer's demand for cheaper material is interesting. However, it was not my intention to compare the two types of wirebars from the economical and even less from the psychological viewpoint. It was my intention—not being a partisan of any make of copper, and not being under obligation to any manufacturer or refiner—merely to show the characteristics of the two types of commercially used wirebars. It is not my fault that the result of this comparison brings me to the definite statement that gas-free copper is a vastly superior raw material for the rolling mill than the old-style tough-pitch copper has been.

The large amount of information that Mr. Bassett was kind enough to contribute on tough-pitch copper certainly helps to give the combined contribution an increased importance in the science of copper.

Mr. Bassett's data prove that certain portions of the tough-pitch wirebar would not satisfy in their hard-drawn state even the requirements established by the A.S.T.M. This, however is a minor factor. It is obvious that no one would take the trouble to industrially roll and draw separately the worst portions of a wirebar. In the usual process the characteristics of the finished wire are equalized, and certainly meet the requirements of the A.S.T.M.

But is this a really valid point? Had the A.S.T.M. been in existence 60 years ago, it might with good reason accept as a standard a wire of 80 per cent conductivity and perhaps of a still lower elongation in 60 in. As it is, the standard mentioned represents merely an arbitrary value, which was agreed upon by the manufacturers that felt certain of being able to meet it "fair or rainy weather." So I refuse to admit that a wire that passed the static tests prescribed by the A.S.T.M. forms a truly good material.

In fact, the enormous amount of kneading to which a wirebar is subjected in the manufacture of wire (99.99 to 99.9999 per cent reduction) cannot fail to produce a wire of good static characteristics. The same applies to iron wire, etc., and were not nature kind enough to permit men to cover up a multitude of sins by using plenty of hard work, we might hardly possess any wrought metal at all.

The use of an inferior raw material to yield an acceptable product can be compared to the action of a builder who has to use two beams of half the size required instead of the needed one, which is not available. He solves the problems as well as he can by joining the two pieces together, by riveting, welding or other method. And for all ends and purposes the compound beam works as if were quite solid, especially in view of the usually high factor of safety used. Dynamically, however, the compound beam is not a solid beam and should the rivets yield under a rapidly vibrating load, the two halves will separate and must from then on act as two beams, with a 50 per cent lower total resistance moment.

The same applies to wires made of tough-pitch wirebars. They may show "an acceptable" combination of characteristics. They may last in service, but they cannot be as resistant dynamically as a wire from a gas-free wirebar can be. It is known beyond doubt that torsion and bending tests always run in favor of the gas-free wire. And while it is not yet experimentally established, I make bold to prophesy that should 100 test pieces be cut from a mile of each type of wire and tension tested, the wires made from a tough-pitch wirebar would show a larger number of stronger variations than the corresponding wires made from a gas-free wirebar.

Again I wish to say that my research for this paper had no other object than to increase our knowledge of the characteristics of copper. Commercial advantages of any company did not enter into my consideration at all.

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